Solicited Proposal for

Task 3.1
of
"Initial Data Analysis of CRPAQS Field Program Measurements"

California Regional $PM_{10}/PM_{2.5}$ Air Quality Study

Submitted to:

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Planning & Technical Support Division
California Air Resources Board
Program Manager
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December 14, 2001

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1. INTRODUCTION

1.1 Goals and Objectives

This data analysis task intends to determine how $PM_{2.5}$ and its chemical components vary in space and time. Specifically, it evaluates the extent to which CRPAQS captured these variations for annual, seasonal, episodic, and individual periods. It examines how much $PM_{2.5}$ is contributed by very nearby emitters, thereby obscuring the degree to which a sampling site accomplished its intended purposes of representing a specific spatial scale or transport regime. Finally, this task identifies locations and sampling periods that add value to the long-term compliance (backbone) network. This will be useful to the ARB and air quality districts as they participate in the U.S. EPA's national network evaluation. A pre-requisite to completing this task is the evaluation of equivalence, comparability, and predictability in Task 1.1. Also needed from Task 1.1 is the data set of $PM_{2.5}$ estimates from particle scattering surrogates. The products of this task will provide guidance to more specific data analyses needed to answer the remaining questions. These analyses are necessary for identifying the potential source types affecting samples that will be quantified as part of Task 4.1.

The objectives of Task 3.1 are:

- Examine the temporal and spatial chemical characteristics of $PM_{2.5}$, PM_{10}, and precursor gas measurements at the anchor and satellite sites.

- Evaluate the zones of influence and spatial homogeneity of PM and precursor concentrations for each of the five anchor sites.

- Determine the zone or representation of anchor sites and backbone sites (selected ones) for long-term research or compliance monitoring.

- Summarize siting characteristics required to represent different spatial scales of influence and to separate primary aerosol contributions from secondary aerosol contributions.

1.2 Background

The spatial and temporal distributions of particulate mass and chemical constituents are essential for understanding source-receptor relationships as well as chemical, physical, and meteorological processes that result in elevated particulate concentrations in central California. There is much variability throughout central California and its major geographical feature, the San Joaquin Valley (SJV). Variability in emissions, meteorology, and terrain are expected to result in substantial differences in PM concentrations and compositions.

The San Joaquin Valley is bordered on the west by the coastal mountain range and on the east by the Sierra Nevada range. These ranges converge at the Tehachapi Mountains at

the southern end of the Valley nearly 200 km south of Fresno, the largest population center for 150 km to the north and south in the central valley. Weather changes with season throughout the year. Spring often experiences small frontal passages with low moisture content resulting in high winds. Summer meteorology is driven by heating over the Mojave desert that creates a thermal low pressure system and a large pressure gradient between the coast and the desert. Fall is influenced by the Great Basin High, with prolonged periods of slow air movement and limited vertical mixing. Mixing depths and ventilation are low in the morning during all seasons and remain low throughout the day during winter. Relative humidities are highest in the winter, with low relative humidities in the summer and fall. During spring, summer, and fall, the typical winds are northwesterly, directed along the Valley axis. This is the predominant non-winter wind-flow pattern both during the day and the night, although it is more sluggish during fall.

Central California emission source categories include: 1) small- to medium-sized point sources (e.g., power stations, incinerators, cement plants, and steam generators); 2) area sources (e.g., fires, wind-blown dust, petroleum extraction operations, cooking, and residential fuel combustion); 3) mobile sources (e.g., cars, trucks, off-road heavy equipment, trains, and aircraft); 4) agricultural and ranching activities (e.g., fertilizers, herbicides, tilling, and livestock); and 5) biogenic sources (e.g., oxides of nitrogen from biological activity in soils and hydrocarbon emissions from plants). Agriculture is the main industry in the central valley, with cotton, alfalfa, corn, safflower, grapes, and tomatoes being the major crops. Cattle feedlots, dairies, chickens, and turkeys constitute most of the animal husbandry in the region. Oil and gas production, refining to the south, waste incineration to the northwest, electrical cogeneration at various locations, transportation, commerce, local government, and light manufacturing constitute the remainder of the economy.

The California Regional $PM_{10}/PM_{2.5}$ Air Quality Study (CRPAQS) is a multiyear effort to understand the causes of elevated suspended particulate concentrations and to evaluate ways to reduce them in central California (Watson et al., 1998). The San Joaquin Valley (SJV) in central California frequently experiences elevated PM_{10} (particles with aerodynamic diameters less than 10 µm) concentrations during the fall and winter months. Past studies (Chow et al., 1992, 1993b, 1996b, 1998) have shown that wintertime particulate matter (PM) concentrations were primarily in the $PM_{2.5}$ size fraction (particles with aerodynamic diameters less than 2.5 µm), while during the remainder of the year PM_{10} consisted of nearly equal parts of $PM_{2.5}$ and coarse particles (PM_{10} minus $PM_{2.5}$).

Receptor model source apportionments showed that the highest $PM_{2.5}$ and PM_{10} concentrations in urban areas during winter contained significant contributions from residential wood combustion, motor vehicle exhaust, and ammonium sulfate ($(NH_4)_2SO_4$), with ammonium nitrate (NH_4NO_3) accounting for 30% to 60% of $PM_{2.5}$ (Magliano et al., 1998a, 1998b, 1999) and nearly half of PM_{10} (Chow et al., 1992). Schauer and Cass (2000) showed that primary emissions from residential wood combustion, vehicle exhaust (including both gasoline- and diesel-powered motor vehicle exhaust), and meat cooking contributed ~80% of fine-particle organic compound mass at the Fresno and Bakersfield areas. $(NH_4)_2SO_4$ and NH_4NO_3 were of secondary origin, formed in the atmosphere from direct emissions of gaseous sulfur dioxide (SO_2), oxides of nitrogen (NO_x), and ammonia (NH_3)

(Watson et al., 1994). When contributions from fugitive dust were large, they always resided in the coarse particle fraction.

Higher annual average $PM_{2.5}$ and PM_{10} concentrations were found in urban areas than in non-urban areas (Chow et al., 1992). While primary (emitted directly) chemical constituents such as elemental carbon (EC) and crustal components (e.g., silicon, iron) displayed spatial variations, the concentrations of inorganic secondary aerosols such as NH_4NO_3 and $(NH_4)_2SO_4$ were much more uniform throughout the valley.

Surface wind speeds during winter in the SJV are very low, often <1 m/sec, and surface wind directions are variable. Surface transport distances estimated from these wind speeds are insufficient to account for the mixing of non-urban NH_3 emissions with urban NO_x emissions for the formation of secondary NH_4NO_3 (Smith and Lehrman, 1994). EC concentrations in the cities are more than three times the non-urban concentrations on the same day (Chow et al., 1993b). These observations suggest that particle concentrations in the SJV are determined by regional-scale interaction of source emissions, chemical transformation, vertical mixing, horizontal transport, and deposition.

A conceptual model is needed to describe how primary particle emissions and gaseous precursors from urban and non-urban areas interact with each other under the stagnant, moist, and foggy conditions often present in the SJV during winter. CRPAQS provided the time-resolved aerosol measurements at urban and non-urban sites, coupled with surface and upper-air meteorological measurements, to formulate this conceptual model and to evaluate the how well the sampling network represented different phenomena observed during the study period.

During the 1988 Valley Air Quality Study at six locations, Chow et al. (1992, 1993b) showed that elevated PM concentrations resulted from a combination of local and regional emissions and meteorology. PM_{10} concentrations of secondary ammonium nitrate were elevated during the winter at all sites. Conversely, concentrations of coarse particle iron, indicative of geologically related dust, were higher under less humid conditions during the summer and fall. Region-wide meteorological and chemical transformation processes influenced the secondary (nitrate and sulfate) components of PM_{10}. Elevated concentrations of coarse-particle dust, however, appear to originate from local emissions such as agricultural- and transportation-related activities, as well as region-wide emissions.

The 1990 San Joaquin Valley Air Quality Study/Atmospheric Utility Signatures, Predictions, and Experiments (SJVAQS/AUSPEX) scrutinized 14 elevated ozone episode days with 4 times/day, 5- to 7-hour sampling at 10 regionally representative locations. Chow et al. (1996b) reported that:

- $PM_{2.5}$ constituted 30% to 70% of PM_{10} mass. Organic carbon was the most abundant species and constituted 25% to 35% of average PM_{10} mass.

- Elevated PM concentrations were found during nighttime (1700 to 2400 PST) and early morning (0000 to 0700 PST) periods.

- Sodium, aluminum, silicon, calcium, and iron were abundant mostly in the coarse particle fraction, consistent with their presence in marine aerosol (sodium) and suspended dust (aluminum, silicon, potassium, calcium, iron). Other trace element concentrations were generally lower in coarse particles than in $PM_{2.5}$. Sulfate, ammonium, organic carbon, and elemental carbon were abundant in the $PM_{2.5}$ fraction; nitrate was abundant in the $PM_{2.5}$ and coarse particle fractions.

- Anion and cation balance showed that sodium sulfate and sodium nitrate were significant in the coarse particle fraction, while ammonium sulfate and ammonium nitrate were significant in the $PM_{2.5}$ fraction.

- The collection of particulate organic carbon on quartz-fiber filters is subject to error from both adsorption of organic gases (positive artifact) and by volatilization of particulate organic carbon (negative artifact) during sampling. Organic carbon measurements on the front quartz-fiber filters may possess a positive bias owing to this artifact, but the cascade impactor data obtained during AUSPEX suggest that the organic carbon measured on the backup quartz-fiber filter may overestimate this artifact in many cases. Additional work is needed to better understand the uncertainties associated with the collection of organic carbon.

- Elevated PM_{10} concentrations occurred sporadically and at individual sites such as Crows Landing and Buttonwillow. Higher wind speed coupled with local activities adjacent to the sampling sites may have resulted in these elevated PM_{10} concentrations.

- Elevated PM_{10} soluble sodium and chloride concentrations were found at northern San Joaquin Valley sites during the episode of 08/03/90 to 08/06/90, and at all California sites during the episode of 08/22/90 to 08/24/90. This is an indication of the influence and extent of transport from coastal sites to inland sites.

The 1995 Integrated Monitoring Study acquired 8 times/day, 3-hour samples at sites in Fresno, Bakersfield, Kern Wildlife Refuge, and Chowchilla. Chow et al. (1999) found that day-to-day variations of $PM_{2.5}$ and PM_{10} and their chemical constituents were influenced by synoptic-scale meteorology and were coherent among the four core sites. Under non-rainy conditions, similar diurnal variations of $PM_{2.5}$ and coarse aerosol were found at the two urban sites, with concentrations peaking during the nighttime hours. Conversely, $PM_{2.5}$ and coarse aerosol peaked during the morning and afternoon hours at the two non-urban sites. Under rainy and foggy conditions, these diurnal patterns were absent or greatly suppressed.

Diurnal PM concentrations were driven by different sources of carbonaceous aerosols at urban sites and by variations in secondary NH_4NO_3 at rural sites. In urban areas, elevated concentrations of primary pollutants (e.g., organic and elemental carbon) during late afternoon and nighttime hours reflected the impact from residential wood combustion and motor vehicle exhaust. During daytime, these concentrations decreased as the mixed layer deepened. Increases of secondary nitrate and sulfate concentrations were found during daylight hours as a result of photochemical reactions. At non-urban sites, the same increases

in secondary aerosol concentrations occurred during daylight hours but with a discernable lag time. Concentrations of primary pollutants also increased at non-urban sites during daytime. These observations are attributed to mixing aloft of primary aerosols and secondary precursor gases in urban areas followed by rapid transport aloft to non-urban areas coupled with photochemical conversion (Chow et al., 1999).

Blanchard et al. (1999) examined spatial variations and reported that primary particle emissions were transported over urban or subregional scales (10 to 30 km) during winter and more than 30 km during fall. Precursor gases and secondary aerosols may have been transported more than 100 km during winter. Average PM_{10} mass and chemical composition varied by more than 20% among central California sites over distances ranging from 4 to 14 km, even though the zones of influence of local sources were less than 1 km. Magliano et al. (1999) found that NH_4NO_3 concentrations were uniform across all sites during both fall and winter. Major site-to-site variations resulted from differences in geological material during fall and from differences in carbonaceous aerosol during winter.

1.3 Evaluation Criteria

The combination of staff, current research projects, facilities, and cost structures of DRI will make this proposal especially attractive to the Technical Committee. The evaluation criteria include: 1) technical approach, 2) expertise of the proposed staff, 3) related previous experience, and 4) cost-effectiveness.

The technical approach is presented in Section 3 of this proposal. This approach provides an overview of PM and precursor gas measurements, sampling locations and durations for the annual program as well as fall and winter intensive studies, and approaches to examining the zones of representations of the different sampling sites.

The principals proposed for DRI are unsurpassed in terms of their demonstrated expertise in this type of study. Dr. Judith Chow at DRI has been a major participant in many California air quality studies including:

- *In California's central valley:* the 1988-89 Valley Air Quality Study (VAQS; Chow et al., 1992, 1993b), 1990 San Joaquin Valley Air Quality Study/Atmospheric Utility Signatures, Predictions, and Experiments (SJVAQS/AUSPEX; Fujita et al., 1995; Chow et al., 1996b), 1995 San Joaquin Valley Integrated Monitoring Study (IMS95; Chow et al., 1998), 1999-2001 CRPAQS aerosol measurements, and 1999-2003 Fresno Supersite Study (Watson et al., 2000; Watson and Chow, 2001a, 2001a);

- *Along the Pacific coast of California:* the 1989 Santa Barbara PM_{10} Study (Chow et al., 1996a) and 1991-92 Bay Area PM_{10} Study (Chow et al., 1995); and

- *In southern and southeastern California:* the 1987 Southern California Air Quality Study (Chow et al., 1994a, 1994b; Fujita et al., 1994; Watson et al., 1994), 1988 Rubidoux/Riverside Neighborhood-Scale Study (Chow et al., 1992),

and 1992-93 Imperial Valley/Mexicali PM_{10} Study (Chow et al., 2000; Chow and Watson, 2001; Watson and Chow, 2001c).

Mr. Steven Kohl has over five years of experience working in and managing DRI's Environmental Analysis Facility. He supervised EAF's staff during the CRPAQS field studies; coordinated field/laboratory logistics during the 14 months of CRPAQS field operations; and has been responsible for assembling, processing, validating, and reporting the Level I aerosol database for CRPAQS and other air quality studies such as the Texas $PM_{2.5}$ Characterization Study, Upper Ohio River Valley Study, Fresno and St. Louis supersite studies, Mid-Atlantic Air Quality Study, and Las Vegas Air Quality Study. The EAF staff worked around the clock during the 2000-01 Christmas/New Year holiday season to ensure that adequate supplies of sampling media and sampling equipment components were available at each of the 53 sampling locations during the 2000-01 CRPAQS winter intensive study period.

DRI's staff have extensive experience in performing spatial and temporal analysis and modeling of concurrent measurements from 20 to 30 sampling locations. The principal investigators and the supporting staff are well acquainted with the sampling, analysis, and modeling aspects of the proposed study.

DRI has completed a number of studies (such as the VAQS, SJVAQS/AUSPEX, IMS95, Las Vegas PM_{10} Study, Imperial Valley/Mexicali zone of representation study, and Mexico City zone of influence study) that are similar to the one proposed here. The proposed team demonstrates experience and participation in nearly every one of the major air quality studies conducted over the past two decades. The principal investigator's experience includes major roles in over a dozen major aerosol and visibility monitoring studies that have resulted in significant advances in the understanding of air pollution. Methods for data analysis and modeling are specified in the technical approach in Section 3.

DRI's ability to carry out the proposed work within the time and budget constraints is outlined in Section 5. A key to maintaining the schedule is that DRI staff are well acquainted with the aerosol measurements taken in the San Joaquin Valley as well as the sampling site locations and surrounding environs. DRI scientists (Dr. Judith Chow, Dr. John Watson, Dr. Douglas Lowenthal, Dr. John Bowen, Mr. Steven Kohl, Mr. Matt Gonzi, Mr. Dale Crow) have been actively working on field operations, data analysis, and air quality modeling for the Fresno Supersite since May 1999. The objectives of the Fresno Supersite project are to: 1) test, evaluate, and compare non-routine and existing monitoring methods; 2) acquire data bases to evaluate relationships between aerosol properties, co-factors, and observed health endpoints; and 3) support regulatory agencies in the development of cost-effective emissions reduction implementation plans. The Fresno Supersite research, which is funded through a cooperative agreement with the U.S. Environmental Protection Agency (U.S. EPA) and the National Oceanic and Atmospheric Administration (NOAA), is directly related to the data analysis to be performed for CRPAQS; as such, substantial cost benefits can be achieved (as shown in Section 8) if DRI is awarded the CRPAQS data analysis task.

This project can and will be given priority. The key personnel are fully dedicated to this project. They have been involved in air quality measurements in the San Joaquin Valley

for more than a decade, and they have always placed this local interest above other more remote opportunities that have presented themselves. DRI is a state agency and is backed by the University and Community College System of Nevada and the State of Nevada. DRI's financial stability as a unit of the University of Nevada System is healthy, long-term, and growing.

With respect to compensation for contracted services, DRI is a non-profit entity and records no financial gain from revenues collected from this or any other project. DRI's interest in this project derives from the unique opportunities it offers to advance our fundamental knowledge about the spatial scales represented by particle samplers. The project has been budgeted to take advantage of different cost structures of the project team. Though DRI must adhere to certain rules established by the Federal Government for cost recovery, it is amenable to alternative arrangements that reduce costs to the sponsors.

Finally, DRI, as part of the State University System, maintains a policy of non-advocacy. DRI participates only in the research aspects of air pollution studies. Results from these studies are presented objectively to decisionmakers without regard to the sensitivities of special interests or political pressures. DRI enjoys the reputation of working equally well with the U.S. EPA, various state and local agencies, and with commercial interests in the development of technical guidance and databases for regulatory analysis. Wherever possible, DRI collaborates with, rather than competes with, the private-sector environmental consulting industry to obtain the best combination of skills, lowest costs, and greatest benefit to the project sponsor and to DRI's goal of technology transfer between university research and environmental assessment.

2. SCOPE OF WORK

Task 3.1 of the Request for Proposal includes six sub-questions:

- QUESTION 3.1-1 How well do the sites represent their designated site types including human exposure, maximum PM concentrations, and maximum source impacts?

- QUESTION 3.1-2 What are monitoring siting characteristics needed to represent neighborhood, urban, and regional, background, and source-oriented PM concentrations and to evaluate transport between source and receptor areas?

- QUESTION 3.1-3 What differences in characteristics exist for primary and secondary contributions?

- QUESTION 3.1-4 How well does the long-term network represent these characteristics?

- QUESTION 3.1-5 How do contributions from various spatial scales influence concentrations at a receptor site?

- QUESTION 3.1-6 How do these vary in space and time?

The following scope of work is structured to answer each of the questions as noted. Each of these subtasks supplies information to address primary **QUESTION 3: WHAT ARE THE TEMPORAL AND SPATIAL REQUIREMENTS FOR RESEARCH AND COMPLIANCE MONITORING NETWORKS?**

2.1 Task 3.1.1: Assess particle measurement validity.

Document and evaluate ambient measurements from the 5 anchor sites, 53 satellite sites, and 68 backbone sites. Document CRPAQS filter-based measurements from the Level I database and conduct Level II data validation. Evaluate the validity of measurement methods for $PM_{2.5}$, PM_{10}, and precursor gases (i.e., ammonia [NH_3] and nitric acid [HNO_3]) by examining the internal and external consistency of the measurements. Attribute inconsistencies to deviations from measurement assumptions, source emissions, meteorological causes, or unknown reasons. Designate samples that require Level III validation by CMB receptor modeling.

2.2 Task 3.1.2: Perform descriptive data analysis.

addresses: QUESTION 3.1-1. How representative are the sites?
QUESTION 3.1-3. Differences in characteristics of primary and secondary contributions?

Prepare statistical and graphical summaries of precursor gas as well as PM mass and chemical data and identify inconsistencies that require further validation. Examine time series plots of PM and selected chemical components. Examine temporal and spatial distributions of the measurements. Evaluate intersite correlations for mass and major chemical components. Calculate the average material balance for each anchor and satellite site. Compare primary and secondary source attributions to each site in different site types. Prepare spatial pie plots or stacked bar charts of annual, seasonal, and maximum chemical compositions. Interpret these, noting differences and similarities among urban and non-urban locations, between air basins, between seasons, and between high $PM_{2.5}$ and low $PM_{2.5}$ wintertime episodes.

2.3 Task 3.1.3: Specify site zones of representation

addresses: QUESTION 3.1-4. How well does the long-term network represent characteristics of primary and secondary contributions?
QUESTION 3.1-5. What influences concentrations at a receptor site?
QUESTION 3.1-6. How do these vary in space and time?

Compare annual-average PM mass and chemical components from each anchor site with spatial averages from the surrounding satellite sites (bracket by neighborhood, urban, and regional scales). Cluster analysis, spatial contour plots, and geostatistics and kriging will be used to examine spatial uniformity of primary and secondary PM aerosols, their source zones of influence, and receptor zones of representation for the three annual sites (Fresno, Angiola, and Bakersfield) and one fall intensive site (Corcoran). From 5-minute-resolution light scattering measurements, apply the successive moving average method (Watson and Chow, 2001b) to estimate contributions from nearby (10 to 500 m) emitters and create frequency distribution plots of $PM_{2.5}$ or PM_{10} (for fall study) contributed by these nearby emitters. Examine detailed diurnal time series for a selection of samples that show very high nearby contributions and attempt to explain these in terms of local emissions events.

2.4 Task 3.1.4: Siting characteristics.

addresses: QUESTION 3.1-2. What monitoring siting characteristics are needed?

From existing site surveys, create a summary table of site characteristics and compare these with the observed. Summarize the internal and external siting criteria. Examine microinventory (if available), maps of the surrounding geography (4 km^2), visual observations, logs of every-sixth-day area surveys, and any other emission characteristics surrounding each anchor site. Determine the extent of meteorological and source influences on standard exceedance days and in different seasons. Summarize findings and, based on results from the previous tasks, determine the conditions under which each site represented its intended purpose and the conditions under which it deviated from those purposes. Generalize these observations to refine siting characteristics required for different spatial scales of representation at a given site.

3. TECHNICAL APPROACH

The CRPAQS aerosol monitoring network (shown in Figure 3.1-1) is supplemented by long-term compliance monitoring sites (shown in Figure 3.1-2). Measurements of precursor gases and PM taken during CRPAQS included: 1) gaseous NH_3 and HNO_3 by the denuder difference method with DRI medium-volume sequential gas samplers (SGS) at the anchor sites; 2) $PM_{2.5}$ and NH_3 by DRI sequential filter samplers (SFS) equipped with Bendix 240 cyclone inlets and preceding nitric acid denuders at the anchor sites; and 3) $PM_{2.5}$, PM_{10}, and NH_3 by battery-powered Airmetrics Minivol samplers at the satellite sites. $PM_{2.5}$ and PM_{10} mass, filter transmission (b_{abs}), 40 elements (Na to U; Watson et al., 1999), ions (Cl^-, NO_3^-, $SO_4^=$, Na^+, K^+, NH_4^+; Chow and Watson, 1999), volatilized NO_3^-, and seven-fraction organic and elemental carbon were acquired.

Measurements of gaseous and particulate organic compounds included: 1) 123 volatile organic compounds (VOCs) from C_2 to C_{12} by canister sampling and gas chromatography/mass spectrometry (GC/MS) analysis, 2) 63 VOCs from C_8 to C_{20} by Tenax-TA cartridge sampling with analysis by the thermal desorption/cryogenic preconcentration method followed by high-resolution gas chromatography separation and flame ionization detection and/or combined mass spectrometry/Fourier transform infrared detection, 3) 14 carbonyl compounds by dinitrophenylhydrazine (DNPH) cartridge sampling and high-performance liquid chromatography analysis, and 4) 151 semivolatile organic compounds (SVOCs) and particulate organics sampled with DRI organic sampling systems at 4 anchor sites (Angiola, Bethel Island, Fresno, and Sierra Foothill) and with Minivol samplers equipped with Teflon-impregnated glass-fiber filters at the 20 satellite sites and analyzed by gas chromatography/mass spectrometry. Table 3.1-1 summarizes measurements acquired from the CRPAQS network, and Table 3.1-2 summarizes measurements from the ARB backbone network.

The annual anchor network includes 14 months of daily $PM_{2.5}$ sampling between 12/03/99 and 02/03/01 at two major urban centers (Fresno [FSF] and Bakersfield [BAC]) to represent community human exposure, and at one intrabasin gradient and vertical gradient site (Angiola [ANGI]) located in a flat field ~85 km south/southeast of Fresno to represent environments with minimal influences from urban or non-urban sources. Two additional anchor sites (Bethel Island [BTI] and Sierra Foothill [SNFH]) were added during the 15-day, 5 times/day winter intensive program for both $PM_{2.5}$ and gaseous NH_3 and HNO_3 measurements. Measurements of VOCs (C_2 to C_{20}) and carbonyls were taken 4 times/day during the winter intensive program at 4 anchor sites (Angiola, Bethel Island, Fresno, and Sierra Foothill). To achieve adequate loadings for heavy hydrocarbons, SVOCs and particulate organics were sampled 2 times/day at the Angiola, Bethel Island, and Sierra Foothill anchor sites and 4 times/day at the Fresno anchor site during the winter intensive.

The satellite network included annual, fall intensive, and winter intensive sampling programs at a total of 53 sites in 8 categories defined by environmental characteristics surrounding the sites (as noted in Table 3.1-1) and included 18 community exposure sites, 11 emissions source dominated sites, 9 visibility sites, 11 intrabasin gradient sites, 2 vertical

Figure 3.1-1. Map of monitoring sites in the CRPAQS network (the fall intensive study's 11 PM_{10} sites are not shown).

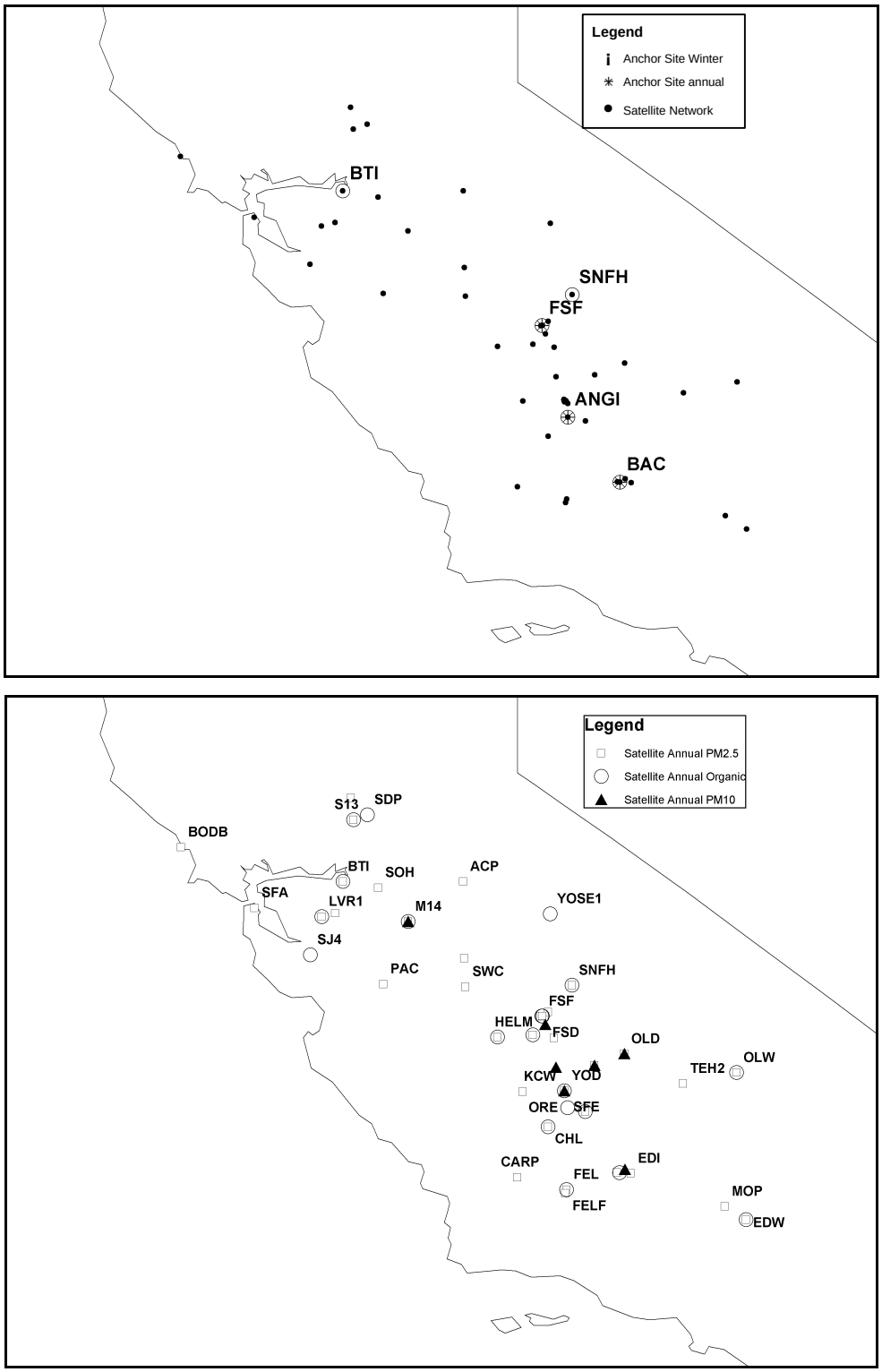


Figure 3.1-2. ARB backbone $PM_{2.5}$ network with Federal Reference Method (FRM) mass measurement and chemical speciation sites. IMPROVE visibility sites are separately designated. The heavy continuous line represents the modeling domain, while the light continuous line represents the annual and winter measurement domain.

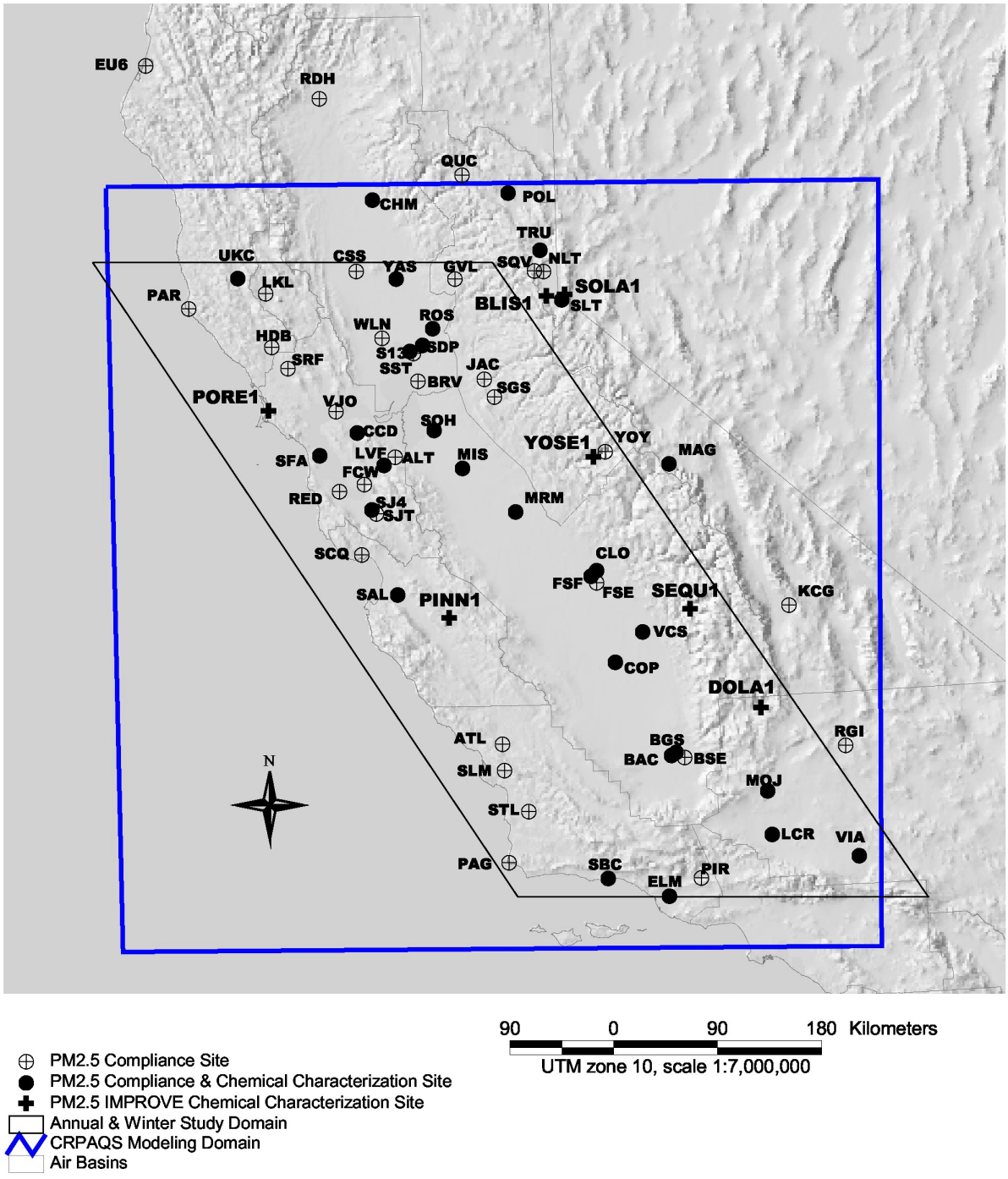


Table 3.1-1. Summary of CRPAQS anchor and satellite site aerosol measurements.[a]

			ANCHOR SITES		SATELLITE SITES[b]							
			Sampling Period		Filter Pack					Sampling Period		
Site Code	**Site Name**	**Site Type**	Annual[c]	Winter Intensive[d]	$PM_{2.5}$		$PM_{2.5}$ Organics	PM_{10}		Annual[e]	Fall Intensive[f]	Winter Intensive[g]
					T/C	q/n	TIGF	T/c	Q/n			
		Minivol module –>			*A* [h]	*B* [i]	*D* [j]	*g* [k]	*h* [l]			
ACP	Angels Camp	Intrabasin Gradient			FTC	FQN				X		X
ALT1	Altamont Pass[m]	Interbasin Transport			FTC					X		X
ANGI	Angiola-ground level	Intrabasin Gradient, Vertical Gradient, Visibility	X	X			TIGF			X		
BAC	Bakersfield-5558 California Street	Community Exposure, Visibility	X	X			TIGF			X		
BGS	Bakersfield-1120 Golden State	Community Exposure						TTC	TQN	(X)		
BODG	Bodega Marine Lab	Boundary/Background			FTC	FQN				X		X
BRES	BAC-Residential	Source- woodburning			FTC	FQN				X		X
BTI	Bethel Island	Interbasin Transport		X	FTC	FQN	TIGF			X		
CARP	Carrizo Plain[m]	Intrabasin Gradient, Visibility			FTC					X		
CHL	China Lake	Visibility			FTC	FQN	TIGF			X		
CLO	Clovis	Community Exposure			FTC	FQN				X		X
CO5	Corcoran Railroad Shoulder	Source - Railroad/ Unpaved Shoulder						TTC			X	
COP	Corcoran-Patterson Avenue	Community Exposure			FTC	FQN	TIGF	TTC	TQN	(X)	X	X
DAIP	Dairy Road - Paved	Source - Paved Road						TTC			X	
DAIU	Dairy Road - Unpaved	Source-Unpaved Road						TTC			X	
EDI	Edison[m]	Intrabasin Gradient			FTC					X		X
EDW	Edwards Air Force Base	Intrabasin Gradient, Visibility			FTC	FQN	TIGF			X		
FEDL	Feedlot or Dairy	Source - Cattle			FTC	FQN	TIGF			X		X
FEL	Fellows	Source- Oilfields			FTC	FQN	TIGF			X		X
FELF	Foothills above Fellows	Intrabasin Gradient			FTC	FQN				X		X
FREM	Fresno MV	Source - Motor Vehicle			FTC	FQN				X		X
FRES	Residential area near FSF, with woodburning	Source - Woodburning			FTC	FQN	TIGF			X		X
FSD	Fresno Drummond	Community Exposure						TTC	TQN	(X)		
FSF	Fresno-3425 First Street	Community Exposure, Visibility	X	X			TIGF			X		
GRA	Grain Elevator	Source - Grain Elevators						TTC	TQN		X	
GRAS	Grain Elevator South	Source - Zone of Influence						TTC	TQN		X	
H43	Highway 43	Southern Boundary						TTC	TQN		X	
HAN	Hanford-Irwin St.	Community Exposure and Fall Northern Boundary						TTC	TQN	(X)	X	
HELM	Agricultural fields/Helm-Central Fresno County	Intrabasin Gradient			FTC	FQN	TIGF			X		X
KCW	Kettleman City[m]	Intrabasin Gradient			FTC					X		X
LVR1	Livermore - New site	Interbasin Transport			FTC	FQN	TIGF			X		X
M14	Modesto 14th St.	Community Exposure			FTC	FQN	TIGF	TTC	TQN	(X)		X

Table 3.1-1. (continued)

			ANCHOR SITES		SATELLITE SITES[b]							
			Sampling Period		Filter Pack					Sampling Period		
Site Code	**Site Name**	**Site Type**	Annual[c]	Winter Intensive[d]	$PM_{2.5}$		$PM_{2.5}$ Organics	PM_{10}		Annual[e]	Fall Intensive[f]	Winter Intensive[g]
					T/C	q/n	TIGF	T/c	Q/n			
		Minivol module –>			*A* [h]	*B* [i]	*D* [j]	*g* [k]	*h* [l]			
MOP	Mojave-Poole	Community Exposure			FTC	FQN				X		
MRM	Merced-midtown	Community Exposure			FTC	FQN				X		X
OLD	Oildale-Manor	Community Exposure			FTC	FQN		TTC	TQN	(X)		
OLW	Olancha	Background			FTC	FQN	TIGF			X		X
ORE	Oregon Avenue	Fall Neighborhood Exposure						TTC			X	
PAC1	Pacheco Pass[m]	Interbasin Transport			FTC					X		
PIXL	Pixley Wildlife Refuge	Rural, Intrabasin Gradient			FTC	FQN	TIGF			X		X
PLE	Pleasant Grove (north of Sacramento)	Intrabasin Gradient			FTC	FQN				X		
S13	Sacramento-1309 T Street	Community Exposure			FTC	FQN	TIGF			X		X
SDP	Sacramento-Del Paso Manor	Community Exposure					TIGF			X		
SELM	Selma(south Fresno area gradient site)	Community Exposure			FTC	FQN				X		X
SFA	San Francisco - Arkansas	Community Exposure			FTC	FQN				X		
SFE	Santa Fe Street	Source - Cotton Handling						TTC	TQN		X	
SJ4	San Jose-4th Street	Community Exposure					TIGF			X		
SNFH	Sierra Nevada Foothills	Vertical Gradient, Intrabasin Gradient, Visibility		X	FTC	FQN	TIGF			X		
SOH	Stockton-Hazelton	Intrabasin Gradient			FTC	FQN				X		X
SWC	SW Chowchilla	Interbasin Transport			FTC	FQN				X		X
TEH2	Tehachapi Pass[m]	Interbasin Transport, Visibility			FTC					X		X
VCS	Visalia Church St.	Community Exposure			FTC	FQN		TTC	TQN	(X)		X
YOD	Yoder Street	Fall Northern Edge of Source Area						TTC			X	
YOSE1	Yosemite National Park-Turtleback Dome	Boundary/Background, Visibility					TIGF			X		
			-------	-------	-------	-------	-------	-------	-------	-------	-------	-------
		Total Number of Sites	3	5	35	29	20	16	11	44	11	25
	18	community exposure sites (SDP, S13, SJ4, SFA, MRM, M14, CLO, FSF, SELM, VCS, HAN, COP, FSD, BGS, OLD, BAC, MOP, and ORE)										
	11	emissions source dominated sites (FRES, FREM, FEDL, GRA, GRAS, SFE, BRES, FEL, CO5, DAIP, and DAIU)										
	9	visibility sites (YOSE1, SNFH, FSF, ANGI, CHL, BAC, CARP, TEH2, and EDW)										
	11	intrabasin gradient sites (PLE, ACP, SOH, SNFH, HELM, KCW, ANGI, PIXL, EDI, FELF, and EDW)										
	2	vertical gradient sites (SNFH and ANGI)										
	1	intrabasin transport site (ACP)										
	6	interbasin transport sites (BTI, ALT1, LVR1, PAC1, SWC, and TEH2)										
	7	boundary/background sites (BODG, YOSE1, HAN, OLW, H43, PIXL, and YOD)										

Table 3.1-1. (continued)

(X) Includes the seven PM_{10} sites operated during the annual program.

[a] Teflon-membrane filter samples were analyzed for mass by gravimetry, filter transmission (b_{abs}) by densitometry, and elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Mo, Pd, Ag, Cd, In, Sn, Sb, Ba, La, Au, Hg, Tl, Pb, and U) by x-ray fluorescence (Watson et al., 1999); quartz-fiber filter samples were analyzed for anions (Cl^-, NO_3^-, $SO_4^=$) by ion chromatography (Chow and Watson, 1999), ammonium by automated colorimetry, water-soluble Na^+ and K^+ by atomic absorption spectrophotometry, and 7-fraction organic and elemental carbon (OC1 combusted at 120 °C, OC2 at 250 °C, OC3 at 450 °C, OC4 at 550 °C, EC1 at 550 °C, EC2 at 700 °C, and EC3 at 800 °C with pyrolysis correction) by thermal/optical reflectance (Chow et al., 1993a, 2001); citric-acid-impregnated filter samples were analyzed for ammonia by automated colorimetry; and sodium-chloride-impregnated filters were analyzed for volatilized nitrate by ion chromatography.

[b] Sampling with battery-powered Minivol samplers (Airmetrics, Eugene, OR) equipped with $PM_{10}/PM_{2.5}$ (in tandem) or PM_{10} inlets at a flow rate of 5 L/min.

[c] Anchor site annual sampling program used DRI medium-volume sequential filter samplers (SFS) equipped with Bendix 240 cyclone $PM_{2.5}$ inlets and preceding anodized aluminum nitric acid denuders. Sampling was conducted daily, 24 hours/day (midnight to midnight) from 12/02/99 to 02/03/01 at a flow rate of 20 L/min. Two filter packs were used for sampling: 1) each Teflon/citric acid filter pack consists of a front Teflon-membrane filter (for mass, b_{abs}, and elemental analyses) backed up by a citric-acid-impregnated cellulose-fiber filter (for ammonia), and 2) each quartz/NaCl filter pack consists of a front quartz-fiber filter (for ion and carbon analyses) backed up by a sodium-chloride-impregnated cellulose-fiber filter (for volatilized nitrate).

[d] Anchor site winter intensive sampling included both SFS for $PM_{2.5}$ sampling and sequential gas samplers (SGS) for ammonia and nitric acid sampling by denuder difference on 15 forecast episode days (12/15/00 to 12/18/00, 12/26/00 to 12/28/00, 01/04/01 to 01/07/01, and 01/31/01 to 02/03/01). The two SGS were equipped with: 1) citric-acid-coated glass denuders and quartz-fiber filters backed up by citric-acid-impregnated cellulose-fiber filters for ammonia (NH_3); and 2) anodized aluminum denuders and quartz-fiber filters backed up by sodium-chloride-impregnated cellulose-fiber filters for nitric acid (HNO_3). VOCs and carbonyls were sampled 4 times/day (0000-0500, 0500-1000, 1000-1600, and 1600-2400) at 4 anchor sites (Angiola, Fresno, Bethel Island, and Sierra Foothill). Heavy hydrocarbons were sampled with Tenax and PUF/XAD samplers 4 times/day (0000-0500, 0500-1000, 1000-1600, and 1600-2400) at the Fresno anchor site and 2 times/day (0500-1600 and 1600-next day 0500) at the Bethel Island, Sierra Foothill, and Angiola anchor sites.

C_2 to C_{12} volatile organic compound (VOC) samples were acquired with canister samplers and analyzed by Dr. Reinhold Rasmussen at the Oregon Graduate Institute of Science and Technology, Portland, OR, using gas chromatography with mass spectrometry to determine concentrations of 123 VOCs:

propene	4-methyl-1-pentene	1-methylcyclopentene	2,3-dimethylhexane	n-nonane	indene
propane	3-methyl-1-pentene	benzene	2-methylheptane	isopropylbenzene	1,3-diethylbenzene
isobutane	cyclopentane	3,3-dimethylpentane	4-methylheptane	isopropylcyclohexane	1,4-diethylbenzene
1,3-butadiene	2,3-dimethylbutane	cyclohexane	3-methylheptane	2,6-dimethyloctane	n-butylbenzene
n-butane	methyl-t-butylether	4-methylhexene	2,2,5-trimethylhexane	alpha-pinene	1,2-diethylbenzene
methanol	2-methylpentane	2-methylhexane	octene-1	3,6-dimethyloctane	1,3-dimethyl-4-ethylbenzene
t-2-butene	2,2-dimethylpentane	2,3-dimethylpentane	1,1-dimethylcyclohexane	n-propylbenzene	isopropyltoluene
1&2-butyne	3-methylpentane	cyclohexene	n-octane	m-ethyltoluene	nonanal
c-2-butene	2-methyl-1-pentene	3-methylhexane	2,3,5-trimethylhexane	p-ethyltoluene	1-undecene
3-methyl-1-butene	1-hexene	1,3-dimethylcyclopentane	2,4-dimethylheptane	1,3,5-trimethylbenzene	n-undecane
ethanol	n-hexane	3-ethylpentane	4,4-dimethylheptane	o-ethyltoluene	1,2,4,5-tetramethylbenzene
isopentane	t-3-hexene	1-heptene	2,6-dimethylheptane	octanal	1,2,3,5-tetramethylbenzene
1-pentene	t-2-hexene	2,2,4-trimethylpentane	2,5-dimethylheptane	beta-pinene	1,2,3,4-tetramethylbenzene
2-methyl-1-butene	2-methyl-2-pentene	t-3-heptene	3,3-dimethylheptane	1-decene	2-methylindan
n-pentane	cis-3-methyl-2-pentene	n-heptane	ethylbenzene	1,2,4-trimethylbenzene	1-methylindan
isoprene	c-3-hexene	2,4,4-trimethyl-1-pentene	m- & p-xylene	n-decane	1-dodecene
t-2-pentene	c-2-hexene	methylcyclohexane	2-methyloctane	isobutylbenzene	naphthalene
c-2-pentene	trans-3-methyl-2-pentene	2,5-diemthylhexane	3-methyloctane	sec-butylbenzene	n-dodecane
2-methyl-2-butene	methylcyclopentane	2,4-diemthylhexane	styrene	1,2,3-trimethylbenzene	
2,2-dimethylbutane	2,4-dimethylpentane	2,3,4-trimethylpentane	o-xylene	limonene	
cyclopentene	2,2,3-trimethylbutane	toluene	1-nonene	indan	

C_8 to C_{20} volatile organic compound samples were acquired with glass cartridges filled with Tenax-TA (a polymer of 2,6-diphenyl-p-phenylene oxide) solid adsorbent and analyzed by the thermal desorption/cryogenic preconcentration method followed by high-resolution gas chromatography separation and flame ionization detection and/or combined mass spectrometry/Fourier transform infrared detection for 63 VOCs:

1,2,4,5-tetramethylbenzene	1-methyl-4-(1-methylethyl)benzene	1,3-diethylbenzene	2,3-dihydroindene (indan)	1-methyl-3-(1-methylethyl)benzene
1(1,1-dimethylethyl)3-5-dimethylbenzene	1,4-diethylbenzene	(1-methylpropyl)benzene	1,2,3,5-tetramethylbenzene	n-pentylbenzene
(1-methylethyl)benzene	1,2-diethylbenzene	1,2,3,4-tetramethylbenzene	1-methyl-2-(1-methylethyl)benzene	(2-methylpropyl)benzene

Table 3.1-1. (continued)

1-methyl-2-ethylbenzene
1-methyl-3-ethylbenzene
1-methyl-4-ethylbenzene
4-methylindan
2-methylindan
5-methylindan
1,3-dimethyl-4-ethylbenzene
1,2-dimethyl-3-ethylbenzene
1,3-dimethyl-5-ethylbenzene
1,2-dimethyl-4-ethylbenzene
1-methyl-2-n-propylbenzene
1-methyl-3-n-propylbenzene
1-methyl-4-n-propylbenzene
1-methyl-2-n-butylbenzene
1,4-dimethyl-2-ethylbenzene
1,3-dimethyl-2-ethylbenzene
1-ethyl-2-n-propylbenzene
1,3-di-n-propylbenzene
2-methylnaphthalene
1-methylnaphthalene
hexanal
heptanal
octanal
nonanal
decanal
undecanal
dodecanal
tridecanal
Tetradecanal
Pentadecanal
Hexadecanal
Octadecanal
2-furaldehyde
benzaldehyde
acetophenone
2,5-dimethylbenzaldehyde
ethanone-1(3-methoxyphenol)
t-2,4-decadienal
Undecane
dodecane
tridecane
tetradecane
pentadecane
hexadecane
heptadecane
octadecane
nonadecane
eicosane

Carbonyl samples were acquired with AtmAA sequential carbonyl samplers and analyzed by Dr. Kochy Fung at AtmAA Environmental Consultants, Calabasas, CA, using high-performance liquid chromatography to determine concentrations of 14 carbonyls (formaldehyde, acetaldehyde, acetone, acrolein, propanal, crotonal, methyl ethyl ketone, methacrolein, butanal, pentanal, glyoxal, hexanal, benzaldehyde, and m-tolualdehyde). Particulate and semivolatile organic compound samples were acquired with DRI Organic Sampling System samplers on Teflon-impregnated glass fiber filters backed up with a PUF/XAD-4/PUF sandwich solid adsorbents and analyzed by gas chromatography with mass spectrometry for 151 particulate and semivolatile VOCs:

Naphthalene
2-menaphthalene
1-menaphthalene
2,6+2,7-dimenaphthalene
1,7+1,3+1,6-dimenaphthalene
2,3+1,4+1,5-dimenaphthalene
1,2-dimenaphthalene
1,8-dimenapthalene
Biphenyl
2-methylbiphenyl
3-methylbiphenyl
4-methylbiphenyl
Trimethylnaphthalene Isomers
Ethyl-Methylnaphthalenes
Acenaphthylene
Acenaphthene
phenanthrene
Fluorene
Methylfluorenes Isomers
1-methylfluorene
Methylphenanthrenes Isomers
2-methylphenanthrene
1-methylphenanthrene
3,6-dimethylphenanthrene
1,7-dimethylphenanthrene
Anthracene
9-methylanthracene
fluoranthene
pyrene
Methylpyrene/fluoranthenes
4-methylpyrene
retene
Benzonaphthothiophene
Benz(a)anthracene
7-methylbenz[a]anthracene
Chrysene/triphenylene
Benzo(b+j+k)FL
BeP
BaP
7-methylbenzo[a]pyrene
indeno[123-cd]pyrene
dibenz(ah+ac)anthracene
Benzo(b)chrysene
Benzo(ghi)perylene
coronene
4Hcyclopenta(def)phenanthren
benzo(c)phenanthrene
Perylene
quinoline
dibenzo[a,e]pyrene
dibenzo[a,h]pyrene
dibenzo[a,i]pyrene
dibenzo[a,l]pyrene
dibenz[a,j]acridine
dibenz[a,h]acridine
7H-dibenzo[c,g]carbazole
5-methylchrysene
dibenz[a,h]anthracene
7,12-dimethylbenzanthracene
3-methylcholanthrene
Oxy-PAH
9-fluorenone
Xanthone
Acenaphthenequinone
Perinaphthenone
Anthraquinone
9-anthraldehyde
Benzanthrone
Benz(a)anthracene-7,12-dione
1,4-chrysenequinone
9,10-dihydrobenzo(a)pyren-7(8H)-one
Nitro-PAH
1-Nitronaphthalene
2-Nitronaphthalene
Methylnitronaphthalenes
2-Nitrobiphenyl
4-Nitrobiphenyl
5-Nitroacenaphthene
2-Nitrofluorene
9-Nitroanthracene
1-Nitropyrene
4-Nitropyrene
3-Nitrofluoranthene
7-Nitrobenz(a)anthracene
6-Nitrochrysene
6-Nitrobenzo(a)pyrene
1,8-Dinitropyrene
1,6-Dinitropyrene
1,3-Dinitropyrene

Hopanes&Steranes
18 (H)-22,29,30-trisnorneohopane
17 (H)-22,29,30-trisnorhopane
17 (H)-21 (H)-29-norhopane
17 (H)-21 (H)-hopane
20R,5 (H),14 (H),17 (H)-cholestane
20R,5 (H),14 (H),17 (H)-cholestane
20R&S,5 (H),14 (H),17 (H)-ergostane
20R&S,5 (H),14 (H),17 (H)-sitostane

Carpanes
8 ,13 -Dimethyl-14 -n-butylpodocarpane
8 ,13 Dimethyl-14 -[3'-methylbutyl]podocarpane
n-Alkanoic Acids
octanoic acid
nonanoic acid
decanoic acid
undecanoic acid
dodecanoic acid
tridecanoic acid
tetradecanoic acid
heptadecanoic acid
octadecanoic acid
nonadecanoic acid
eicosanoic acid
Alkanedioic acids
octadecanedioic acid
nonadecanedioic acid
Aromatic acids
benzoic acid
methylbenzoic acid

Alkanes
n-pentadecane
n-hexadecane
n-heptadecane
n-octadecane
n-nonadecane
n-eicosane
n-heneicosane
n-docosane
n-tricosane
n-tetracosane
n-pentacosane
n-hexacosane
n-heptacosane
n-octacosane
farnesane
norpristane
norfarnesane
pristane
phytane

Saturated Cycloalkanes
tridecylcyclohexane
tetradecylcyclohexane
pentadecylcyclohexane
hexadecylcyclohexane
heptadecylcyclohexane
octadecylcyclohexane
nonadecylcyclohexane

Lower priority cycloalkanes
heptylcyclohexane
octylcyclohexane
nonylcyclohexane
decylcyclohexane
undecylcyclohexane
dodecylcyclohexane
eicosylcyclohexane
heneicosycyclohexane

Table 3.1-1. (continued)

[e] Satellite site annual sampling program included every-sixth-day 24-hour sampling at 35 $PM_{2.5}$ sites and 7 PM_{10} sites between 12/02/99 and 02/03/01. Particulate organic compounds were sampled at 20 sites between 02/06/00 and 01/31/01.

[f] Satellite site fall intensive study included 24-hour sampling of PM_{10} on 37 days between 10/09/00 and 11/14/00 at 11 sites. 6 sites (COP, H43, HAN, GRA, GRAS, and SFE) were equipped with both Teflon/citric acid and quartz/NaCl filter packs. 5 sites (CO5, DAIP, DAIU, ORE, and YOD) were equipped with only Teflon/citric acid filter packs.

[g] Satellite site winter intensive study included 24-hour sampling of $PM_{2.5}$ on 13 forecast episode days (12/15/00 to 12/18/00, 12/25/00, 12/27/00, 12/28/00, 01/04/01 to 01/06/01, and 02/01/01 to 02/03/01) at 25 $PM_{2.5}$ sites, with 21 of the sites equipped with both Teflon/citric acid and quartz/NaCl filter packs.

[h] Minivol module A: $PM_{2.5}$ Teflon/citric acid filter packs at 35 satellite sites. Each filter pack consisted of a front Teflon-membrane filter (for mass, b_{abs}, and elements) backed up by a citric-acid-impregnated cellulose-fiber filter (for ammonia).

[i] Minivol module B: $PM_{2.5}$ quartz/NaCl filter packs at 29 satellite sites (same sites as module A but excluding ALT1, PAC1, KCW, EDI, CARP, and TEH2). Each filter pack consisted of a front pre-fired quartz-fiber filter (for ions and carbon) backed up by a sodium-chloride-impregnated cellulose-fiber filter (for volatilized nitrate).

[j] Minivol module D: $PM_{2.5}$ Teflon-impregnated glass-fiber filters (TIGF) at a total of 20 sites (including 3 annual anchor sites [Fresno, Angiola, and Bakersfield], 14 annual satellite sites, the San Jose-4th St. [SJ4] site, the Sacramento-Del Paso Manor [SPP] site, and the Yosemite [YOSE1] site). A total of 61 samples acquired over the yearlong sampling period were composited as one sample and analyzed by gas chromatography with mass spectrometry (GC/MS) for 151 particulate organic compounds as listed in footnote d above.

[k] Minivol module g: PM_{10} Teflon/citric acid filter packs at 16 satellite sites, 4 of which (M14, VCS, COP, and OLD) were collocated with annual $PM_{2.5}$ measurements, and 7 of which (M14, VCS, COP, FSD, BGS, HAN, and OLD) were annual PM_{10} sites. Each filter pack consisted of a front Teflon-membrane filter (for mass, b_{abs}, and elements) backed up by a citric-acid-impregnated cellulose-fiber filter (for ammonia).

[l] Minivol module h: PM_{10} quartz/NaCl filter packs at 16 satellite sites, 4 of which were collocated with annual $PM_{2.5}$ measurements (M14, VCS, COP, and OLD), and 7 of which (M14, VCS, COP, FSD, BGS, HAN, and OLD) were annual PM_{10} sites. Each filter pack consisted of a front quartz-fiber filter (for ion and carbon analyses) backed up by a sodium-chloride-impregnated cellulose-fiber filter (for volatilized nitrate).

[m] One of six sites (ALT1, PAC1, KCW, EDI, CARP, and TEH2) where only Minivol module A Teflon/citric acid filter packs were acquired.

Table 3.1-2. $PM_{2.5}$ mass measurements acquired from the central California backbone network.

Site Code[a]	Site Name	Site Type[a]	Sampling Frequency	$PM_{2.5}$ Sampler[b]	Speciation Sampler[c]
ALT	Altamont Pass-Tracy	S	1 in 3		
ATL	Atascadero-Lewis Ave	C	1 in 6	(X)	
BGS[d]	Bakersfield-1120 Golden State	C	1 in 3	X	S
BAC[d]	Bakersfield-5558 California Ave	C	every day	(X)	S
BLIS1	D.L. Bliss State Park-TRPA	I	1 in 3	I	
BRV	Elk Grove-Bruceville Rd	C	1 in 3		
BSE	Bakersfield-Southeast (410 E. Planz)	C	1 in 3	X	
CCD	Concord-2975 Treat Blvd	C	every day	(X)	S
CHM	Chico-Manzanita Ave	C	1 in 6	X	S
CLO[d]	Clovis-908 N Villa Ave	C	1 in 3	X	S
COP[d]	Corcoran-Patterson Ave	C	1 in 3	X	S
CSS	Colusa-100 Sunrise Blvd	C	1 in 3	X	
DOLA1[e]	Dome Land Wilderness-USFS	I	1 in 3	I	
ELM	El Rio-Mesa School #2	C	1 in 3	X	S
EU6	Eureka-Health Dept	C	1 in 6	X	
FCW	Fremont-Chapel Way	C	1 in 3	X	
FSE	Fresno-Southeast (Pacific College)	C	1 in 3	X	
FSF[d]	Fresno-3425 First Street	C	every day	(X)	S
GVL	Grass Valley-Litton Building Site	C	1 in 6	X	
HDB	Healdsburg-Limeric Lane	C	1 in 6		
JAC	Jackson-201 Clinton Road	C	1 in 3		
KCG	Keeler-Cerro Gordo Road	C	1 in 3	(X)	
LCR	Lancaster-W Pondera Street	C	1 in 3	X	S
LKL	Lakeport-Lakeport Blvd	C	1 in 6	X	
LTY	South Lake Tahoe-Sandy Way	C	1 in 6	(X)	S
LVF	Livermore (793 Rincon Ave.)	C	1 in 3	X	S
MAG	Mammoth Lakes-Gateway HC	C	1 in 3	X	S
M14	Modesto-14th St.	C	1 in 3	X	S
MOJ	Mojave-923 Poole Street	C	1 in 3	X	S
MRM[d]	Merced-Midtown	C	1 in 3	X	S
NLT	North Lake Tahoe-Near Tahoe City (Echo Summit)	C	1 in 3	X	
PAG	Point Arguello	S	1 in 3		
PARN	Point Arena	S	1 in 3		
PINN1	Pinnacles National Monument-NPS	I	1 in 3	I	
PIR	Piru-2 mi SW	S	1 in 3	X	
POL	Portola	C	1 in 3	X	S
PORE1	Point Reyes National Seashore-NPS	I	1 in 3	I	
QUC	Quincy-267 North Church Street	C	1 in 3	X	
RDH	Redding-Health Dept Roof	C	1 in 6	X	
RED	Redwood City	C	1 in 3	X	

Table 3.1-2. (continued)

Site Code[a]	Site Name	Site Type[a]	Sampling Frequency	$PM_{2.5}$ Sampler[b]	Speciation Sampler[c]
RGI	Ridgecrest-Las Flores Ave	C	1 in 3	X	
ROS	Roseville-151 N Sunrise Blvd	C	1 in 6	X	S
S13[d]	Sacramento-1309 T Street	C	every day	X	S
SAL	Salinas	C	1 in 3	X	S
SBC	Santa Barbara-3 W Carillo St	C	1 in 6	X	S
SCQ	Santa Cruz-2544 Soquel Dr	C	1 in 3	X	
SDP[d]	Sacramento-Del Paso Manor	C	some every day, some 1 in 3, some 1 in 6	X	S
SEQU1	Sequoia National Park-NPS	I	1 in 3	I	
SFA[d]	San Francisco-10 Arkansas St	C	1 in 6 except every day from October thru March	X	S
SGS	San Andreas-Gold Strike Road	C	1 in 6	X	
SJ4[d]	San Jose-4th St	C	every day	X	S
SJT	San Jose-528 Tully Road	C	every day	X	
SLM	San Luis Obispo-Marsh St	C	1 in 6	X	
SOH[d]	Stockton-Hazelton St	C	1 in 3	X	S
SOLA1	South Lake Tahoe-TRPA	I	1 in 3	I	
SQV	Squaw Valley-New site	C	1 in 3		
SRF	Santa Rosa-837 Fifth St	C	1 in 3	X	
SST	Sacramento-Health Dept Stockton Blvd	C	every day	X	
STL	Santa Maria-Library (Broadway)	C	1 in 6	X	
TRU	Truckee-Fire Station	C	1 in 3	(X)	S
UKC	Ukiah-County Library	C	1 in 6	X	S
VCS[d]	Visalia-N Church Street	C	1 in 3	X	
VIA	Victorville-Armargosa Road	C	1 in 3	(X)	S
VJO	Vallejo-304 Tuolumne St	C	1 in 3	X	
WLN	Woodland	C	1 in 3	X	
YAS	Yuba City-Almond Street	C	1 in 6	(X)	S
YOSE1	Yosemite National Park-Turtleback Dome	I	1 in 3	I	
YOY	Yosemite National Park-Yosemite Village	C	1 in 3		

[a] C = core SLAMS. S = non-core SLAMS. P = special purpose. I = IMPROVE.

[b] X = $PM_{2.5}$ FRM monitor. (X) = collocated $PM_{2.5}$ FRMs. I = IMPROVE sampler.

[c] S = speciation sampler.

[d] One of 12 sites that are collocated with CRPAQS $PM_{2.5}$ aerosol measurements.

[e] Seasonal operating period.

gradient sites, 1 intrabasin transport site, 6 interbasin transport sites, and 7 boundary/background sites. Detailed site locations, elevations, coordinates are summarized in Table 3.1-3. Descriptions of each site and its surrounding environment will be assembled and incorporated into this table when the site documentation file is completed. The satellite sites were designed to: 1) examine spatial variations of PM concentrations within the study domain, 2) identify potential pollutant transport in the prevailing wind direction, 3) determine the zones of influence of specific emitters (e.g., fugitive dust) on PM loadings in a mixed-land-use area, and 4) evaluate the zones of representation of single-site measurements for community exposure to PM. The satellite sites within the air basin represent middle-scale (0.1 to 0.5 km), neighborhood-scale (0.5 to 4 km), and urban-scale (4 to 100 km) influences around the anchor sites, whereas the inter- or intrabasin gradient sites and boundary/background sites represent urban-scale to regional-scale (100 to 1,000 km) influences.

The annual satellite network consisted of 14 months of every-sixth-day, 24-hour sampling at 53 locations (including 35 $PM_{2.5}$ sites, 20 $PM_{2.5}$ organic compound sites [12 months of sampling between 02/06/00 and 01/31/01 only], and 7 PM_{10} sites). The fall intensive study included daily 24-hour sampling of PM_{10} between 10/09/00 and 11/14/00 at 11 sites. The winter intensive study included daily 24-hour sampling of $PM_{2.5}$ on 13 forecast episode days at 25 sites. $PM_{2.5}$ organic compound samples collected during the annual program were composited to one sample per site for gas chromatography/mass spectrometry analysis of particulate organics.

3.1 Task 3.1.1 – Measurement Validity

As part of the Level II data validation process for aerosol measurements, the following tasks will be performed:

- Sum of Species versus Mass. The sum of individual chemical concentrations for $PM_{2.5}$ or PM_{10} should be less than or equal to the corresponding gravimetrically measured mass. If reconstructed mass exceeds ±20% of measured mass, samples will be reexamined, reanalyzed, and/or flagged as suspect in the database.

- Physical Consistency. The composition of chemical species concentrations measured by different chemical analysis methods are checked. Physical consistency checks include:

  - *Sulfate versus total sulfate:* The ratio of water soluble sulfate measured by ion chromatography (IC) on quartz-fiber filters to total sulfur measured by x-ray fluorescence (XRF) on Teflon-membrane filters should be approximately three. Ratios deviating more than ±10% from three will be reexamined, reanalyzed, and/or flagged as suspect in the database.

  - *Chloride versus chlorine:* The ratio of chloride measured by IC on quartz-fiber filters to chlorine measured by XRF on Teflon-membrane filters should

Table 3.1-3. Summary of CRPAQS sampling site locations, elevations, coordinates.

Site Code	Site Address	Elevation (MSL, m) ±1 m or ±5 m*	Coordinates (north) ± 2”	Coordinates (west) ± 2”
ACP	6850 Studhorse Flat Road, Sonora	373*	N 38° 0’ 21”	W 120° 29’ 29”
ALT1	Flynn Road exit, I-580	350*	N 37° 43’ 3”	W 121° 39’ 37”
ANGI	36078 4th Avenue, Corcoran	60	N 35° 56’ 53”	W 119° 32’ 16”
BAC	5558 CA Ave. #430 (STI) #460 (ARB), Bakersfield	119	N 35° 21’ 24”	W 119° 3’ 45”
BGS	1120 Golden State, Bakersfield	126	N 35° 23’ 9”	W 119° 0’ 42”
BODG	Bodega Marine Lab, 2099 Westside Road, Bodega Bay	17	N 38° 19’ 8”	W 123° 4’ 22”
BRES	7301 Remington Avenue, Bakersfield	117	N 35° 21’ 29”	W 119° 5’ 1”
BTI	5551 Bethel Island Road, Bethel Island	2	N 38° 0’ 23”	W 121° 38’ 31”
CARP	Soda Springs Road, 0.5 mile south of California Valley	598	N 35° 18’ 51”	W 119° 59’ 45”
CHL	Baker Site	684	N 35° 46’ 27”	W 117° 46’ 35”
CLO	908 N. Villa, Clovis	108	N 36° 49’ 10”	W 119° 42’ 59”
CO5	Pole with transformer on E side of RR tracks, just N of Sherman	64	N 36° 5’ 42”	W 119° 33’ 15”
COP	1520 Patterson Ave., Corcoran	63	N 36° 6’ 8”	W 119° 33’ 57”
COP	1520 Patterson Ave., SJVAPCD site	63	N 36° 6’ 8”	W 119° 33’ 57”
DAIP	Pole #GT209662, 2nd pole S of North Street on Dairy Avenue	63	N 36° 6’ 18”	W 119° 34’ 19”
DAIU	Pole #CTC1207297, SE corner of Dairy and Tennent	63	N 36° 6’ 36”	W 119° 34’ 20”
EDI	4101 Kimber Avenue, Bakersfield	118	N 35° 21’ 1”	W 118° 57’ 26”
EDW	North end of Rawinsonde Road, Edwards AFB	724	N 34° 55’ 46”	W 117° 54’ 15”
FEDL	8555 S. Valentine, Fresno (near Raisin City)	76	N 36° 36’ 40”	W 119° 51’ 19”
FEL	Across from 25883 Hwy 33, Fellows	359	N 35° 12’ 9”	W 119° 32’ 45”
FELF	Texaco Pump Site 47-1, Fellows	512*	N 35° 10’ 14”	W 119° 33’ 25”
FREM	Pole #16629, 2253 E. Shields Ave., Fresno	96	N 36° 46’ 48”	W 119° 47’ 0”
FRES	Pole #16962, 3534 Virginia Lane, Fresno	97	N 36° 46’ 59”	W 119° 46’ 6”
FSD	4706 E. Drummond, Fresno	91	N 36° 42’ 20”	W 119° 44’ 29”
FSF	3425 First Street, Fresno	97	N 36° 46’ 54”	W 119° 46’ 24”
GRA	Set of 4 poles just S of Whitley and E of the RR tracks, 30 m W of pole #100	64	N 36° 5’ 51”	W 119° 33’ 19”
GRAS	Pole #534 on NW corner of Otis and Sherman	64	N 36° 5’ 40”	W 119° 33’ 17”
H43	Pole at intersection of Hwy 43 and Santa Fe Avenue/4th Avenue, in grassy triangle	64	N 36° 4’ 18”	W 119° 32’ 10”
HAN	807 S. Irwin St., Hanford	76	N 36° 18’ 53”	W 119° 38’ 38”

Table 3.1-3. (continued)

Site Code	Site Address	Elevation (MSL, m) ±1 m or ±5 m*	Coordinates (north) ± 2”	Coordinates (west) ± 2”
HELM	Near Placer & Springfield	55	N 36° 35’ 26”	W 120° 10’ 38”
KCW	Omaha Avenue 2 miles west of Hwy 41, Kettleman City	69	N 36° 5’ 41”	W 119° 56’ 51”
LVR1	793 Rincon Street, Livermore	138	N 37° 41’ 15”	W 121° 47’ 3”
M14	814 14th Street, Modesto	28	N 37° 38’ 31”	W 120° 59’ 40”
MOP	923 Poole Street, Mojave	832	N 35° 3’ 2”	W 118° 8’ 54”
MRM	2334 M Street, Merced	53	N 37° 18’ 30”	W 120° 28’ 50”
OLD	3311 Manor Street, Oildale	180	N 35° 26’ 17”	W 119° 1’ 1”
OLW	Just to east of Hwy 395	1124	N 36° 16’ 4”	W 117° 59’ 34”
ORE	Cafeteria roof, Mark Twain School, 1500 Oregon Avenue	62	N 36° 5’ 15”	W 119° 33’ 57”
PAC1	Upper Cottonwood Wildlife Area, west of Los Banos	452*	N 37° 4’ 24”	W 121° 13’ 18”
PIXL	Road 88, 1.5 miles north of Avenue 56, Alpaugh	69	N 35° 54’ 49”	W 119° 22’ 33”
PLE	7310 Pacific Avenue, Pleasant Grove	10	N 38° 45’ 58”	W 121° 31’ 9”
S13	1309 T Street, Sacramento	6	N 38° 34’ 6”	W 121° 29’ 36”
SDP	2700 Maryal Drive, Sacramento	26	N 38° 36’ 49”	W 121° 22’ 5”
SELM	7225 Huntsman Avenue, Selma	94	N 36° 34’ 58”	W 119° 39’ 37”
SFA	10 Arkansas St., San Francisco	6	N 37° 45’ 57”	W 122° 23’ 56”
SFE	Pole #T207157 on E side of Santa Fe Avenue, 1 mile N of Hwy 43 intersection	64	N 36° 5’ 2.3”	W 119° 32’ 45”
SJ4	120 N. 4th Street, San Jose	26	N 37° 20’ 23”	W 121° 53’ 19”
SNFH	31955 Auberry Road, Auberry	589*	N 37° 3’ 45”	W 119° 29’ 46”
SOH	1601 E. Hazelton, Stockton	8	N 37° 57’ 1”	W 121° 16’ 8”
SWC	20513 Road 4, Chowchilla	43	N 37° 2’ 53”	W 120° 28’ 18”
TEH2	Near 19805 Dovetail Court, Tehachapi	1229*	N 35° 10’ 4”	W 118° 28’ 55”
VCS	310 Church Street, Visalia	102	N 36° 19’ 57”	W 119° 17’ 28”
YOD	Pole #CTC1039727 on E side of Yoder, just N of Patterson	64	N 36° 6’ 6”	W 119° 33’ 30”
YOSE1	Turtleback Dome	1685*	N 37° 42’ 41”	W 119° 41’ 45”

1. All coordinates are referenced to the NAD83 map datum.
2. Coordinates are reported as read by a Garmin GPS device at the site (model GPSII); accuracy is limited to about ±2” (approximately ±50 meters).
3. Elevations are relative to sea level and were determined from a topo map; accuracy is about ±1 meter for valley and coastal sites, ±5 meters for mountain sites (shown with asterisk*).

be less than one. Ratios exceeding unity will be reexamined, reanalyzed, and/or flagged as suspect in the database.

- *Soluble potassium versus total potassium:* The ratio of water soluble potassium measured by atomic absorption spectrophotometry (AAS) on quartz-fiber filters to total potassium measured by XRF on Teflon-membrane filters should be less than one. Ratios exceeding unity will be reexamined, reanalyzed, and/or flagged as suspect in the database.

- Ammonium Balance. Ammonium nitrate (NH_4NO_3), ammonium sulfate ($[NH_4]_2SO_4$), and ammonium bisulfate (NH_4HSO_4) are the most likely nitrate and sulfate compounds to be found in central California. Some sodium nitrate ($NaNO_3$) and/or sodium sulfate (Na_2SO_4) are also present, but these are more abundant during summertime marine air conditions (Chow et al., 1996a). Ammonium can be calculated based on the stoichiometric ratios of the different compounds and compared with what was measured. This process verifies the validity of the ammonium measurements and provides insight on the extent of ammoniation.

- Anion and Cation Balance. Anions, such as chloride, nitrate, and sulfate acquired by IC, are compared with cations such as soluble sodium and potassium acquired by AAS and ammonium acquired by automated colorimetry (AC). The anion and cation balance should be highly correlated and most of the cations should be balanced with anions on a molar equivalent basis. A closure in the ion balance assures that adequate anions and cations were measured during the study.

3.2 Task 3.1.2 – Descriptive Data Analysis

The objectives for descriptive data analysis are as follows: 1) identify similarities and differences between $PM_{2.5}$ and PM_{10} mass and chemical species; 2) determine where and when excessive $PM_{2.5}$ and PM_{10} concentrations occur; 3) depict temporal and spatial variations in $PM_{2.5}$, PM_{10}, and precursor gas measurements; and 4) evaluate differences in characteristics of primary and secondary contributions. Data used in these analyses include the following: 1) $PM_{2.5}$ SFS data; 2) $PM_{2.5}$ and PM_{10} Minivol sampler data; 3) $PM_{2.5}$ data from Federal Reference Method (FRM) samplers in ARB's compliance network (only for selected sites [e.g., Sacramento, Stockton, San Francisco, San Jose, Modesto, Clovis, Visalia, Corcoran, and Mojave] that are surrounded with satellite monitors); and 4) $PM_{2.5}$ and PM_{10} emission rate/activity data and meteorological data from CRPAQS.

Descriptive data analysis activities include:

- Statistical summaries of average, maximum, and minimum values of aerosol variables for 3-, 5-, 8-, and 24-hour periods.

- Time series plots of $PM_{2.5}$, PM_{10}, and selected chemical components with examination to select representative episodes for more intensive analysis.

- Spatial pie plots or stacked bar charts of chemical composition for annual-average, seasonal, and maximum concentrations.

- Correlations between $PM_{2.5}$ and PM_{10} mass and chemical composition measurements.

The product of this analysis will be a quantitative overview of air quality during the study period. This analysis will allow more complex and time-consuming activities to be focused on those cases that provide the best examples for developing emissions reduction strategies.

$PM_{2.5}$ and PM_{10} mass concentrations from the time series plots will be examined to find features such as: 1) $PM_{2.5}/PM_{10}$ fractions (where data are available); 2) high concentration days and sites to determine the nature of the elevated concentrations in terms of local neighborhood vs. valley-wide events; and 3) periods of pollutant build-up and clearing.

During the annual program, 24-hour PM_{10} concentrations exceeded the 150 $\mu g/m^3$ National Ambient Air Quality Standards (NAAQS) 9 times at 5 of 7 satellite sites over the 14-month sampling period. As shown in Table 3.1-4, the maximum PM_{10} concentration was 207 $\mu g/m^3$ reported on 01/04/01 at the BGS site (1120 Golden State St., Bakersfield). The

Table 3.1-4. Summary of 24-hour PM_{10} mass concentrations during CRPAQS.

	Site	Number of samples ≥ 50[a] $\mu g/m^3$	Number of samples ≥ 150[b] $\mu g/m^3$	Site Average ± Standard Deviation	Maximum Concentration	Date of Maximum
Satellite Site Annual Program PM_{10} (12/03/99 to 02/03/01)	BGS	19	2	51.4 ± 38.9	207.6	01/04/01
	COP	18	0	43.6 ± 30.7	140.9	12/23/99
	FSD	21	3	46.4 ± 37.0	168.2	12/23/01
	HAN	19	2	46.8 ± 36.6	182.9	12/11/99
	M14	14	0	32.8 ± 25.6	120.1	01/10/00
	OLD	11	1	41.7 ± 34.1	195.2	04/04/01
	VCS	20	0	44.8 ± 31.2	147.1	01/10/00
Satellite Site Fall Intensive Study PM_{10} (10/09/00 to 11/14/00)	C05	19	0	54.9 ± 27.8	106.9	11/04/00
	COP	15	0	46.7 ± 26.8	100.5	10/09/00
	DAIP	16	0	48.2 ± 26.5	96.3	10/09/00
	DAIU	18	0	45.9 ± 26.4	99.0	10/09/00
	GRA	19	0	55.8 ± 29.2	124.5	10/23/00
	GRAS	17	0	55.7 ± 26.1	107.0	10/23/00
	H43	14	0	46.4 ± 24.2	85.3	10/23/00
	HAN	14	0	45.4 ± 27.1	103.7	11/04/00
	ORE	16	0	44.7 ± 25.1	90.6	11/04/00
	SFE	22	0	62.8 ± 32.9	123.2	11/07/00
	YOD	19	0	48.5 ± 28.3	103.4	10/10/00

[a] 24-hr PM_{10} standard set by State of California.

[b] 24-hr PM_{10} standard set by National Ambient Air Quality Standards.

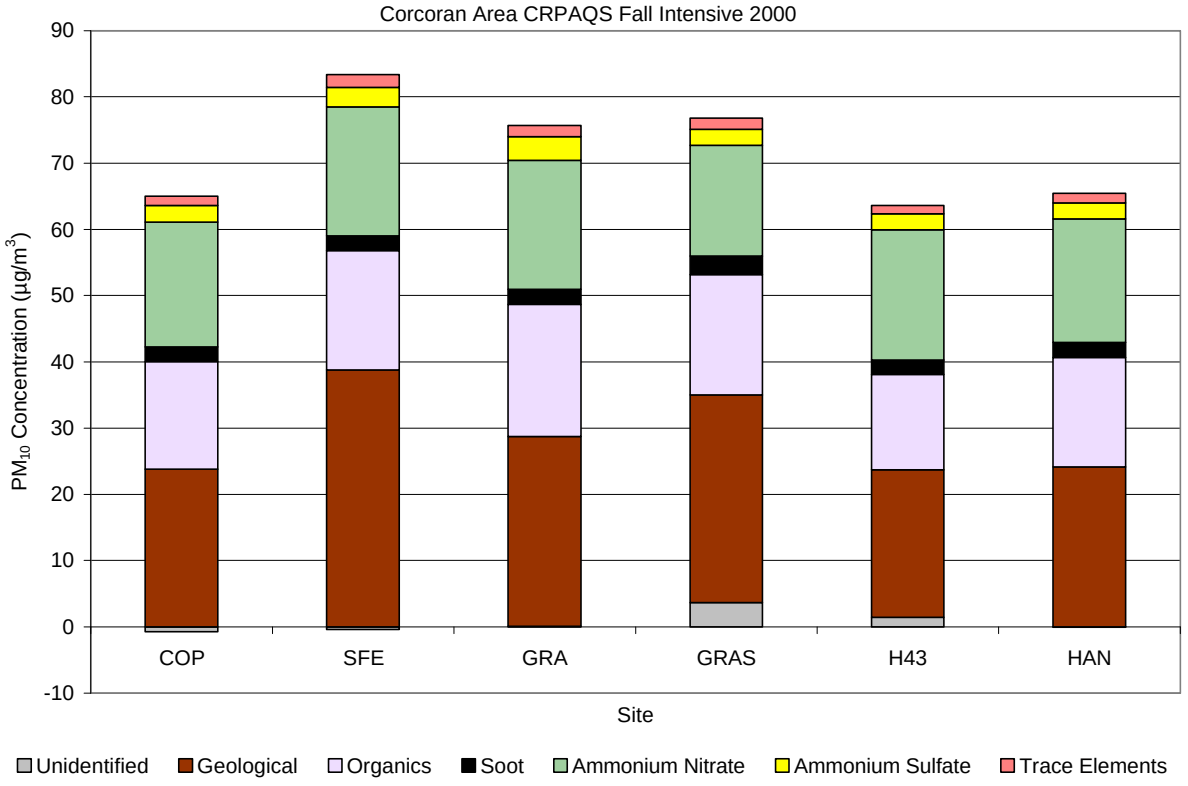
24-hour California state standard of 50 $\mu g/m^3$ was exceeded at all sites on 18% to 31% of the days. PM_{10} concentrations were lower during the fall intensive period, with the maximum concentration of 124 $\mu g/m^3$ found on 10/23/00 at the GRA source-oriented (grain elevator) site, but California's state standard was exceeded 42% to 63% of the time at the 11 fall intensive sites. The average 14-month PM_{10} concentration at the Corcoran site was 42.9 $\mu g/m^3$, which is ~10% lower than the 37-day average from the fall intensive study. However, the highest 24-hour $PM_{2.5}$ concentrations were 179 $\mu g/m^3$ occurring at the Edison (EDI) site on 01/05/01 and 176 $\mu g/m^3$ at the Fresno motor vehicle (FREM) site on 01/01/01. These levels exceed twice the 24-hour $PM_{2.5}$ NAAQS of 65 $\mu g/m^3$. Further investigation will be made to understand the causes of these elevated concentrations.

Statistical summaries will be used to identify maximum PM mass and chemical concentrations at each site and to compare annual and seasonal averages among sites. Material balances will be used to reconstruct $PM_{2.5}$ and PM_{10} mass by the major PM categories. $PM_{2.5}$ and PM_{10} can be estimated (Solomon et al., 1989) by the following steps: 1) sum the aluminum, silicon, calcium, and iron oxides (i.e., [1.89 × aluminum] + [2.14 × silicon] + [1.4 × calcium] + [1.43 × iron]) to estimate the geological material; 2) multiply average organic carbon concentrations by 1.4 to account for unmeasured hydrogen and oxygen in organic material; 3) multiply non-volatilized nitrate by 1.29 to calculate ammonium nitrate; 4) multiply sulfate by 1.38 to calculate ammonium sulfate; and 5) add the concentrations of remaining elemental species without double-counting geological species, sodium, magnesium, and total sulfur.

Figure 3.1-3 displays average PM_{10} material balances for six sites during the fall intensive study. The height of each stacked bar represents the measured PM mass concentration. Negative unexplained mass is shown when the material balance exceeds the measured mass concentration. In most cases the material balance explains most of the measured PM_{10} mass. PM_{10} geological material is by far the largest contributor to PM_{10} mass, accounting for 34% to 46% of PM_{10} mass. Data from sampling sites near cotton handling (SFE) and grain elevator (GRA and GRAS) operations show greater-than-typical geological and PM_{10} mass concentrations within the neighborhood-scale domain. The highway site near the airport (H43) did not exhibit elevated carbon concentrations. PM_{10} organics and secondary NH_4NO_3 exhibited more uniform distributions, accounting for 22% to 26% and 17% to 24% of PM_{10} mass, respectively. Material balances will be generated for each site to evaluate primary and secondary aerosol attributions and to compare source attributions to annual and seasonal averages on maximum concentration days.

Correlation matrices can be applied to resolve spatial and temporal patterns of PM mass and major chemical constituents. These correlation coefficients show which concentrations changed in the same way over time. Coefficients that exceed 0.80 represent a fairly strong covariation; coefficients between 0.50 and 0.80 represent a moderate covariation; and coefficients of less than 0.50 are not considered to be physically significant (though they may be statistically significant). High correlation coefficients are observed when pairs of variables originate from the same source, are equally affected by transport and dispersion, or undergo related chemical transformations. Sites in close proximity to each other often form a high correlation cluster, indicative of area-wide phenomena.

Figure 3.1-3. Material balance of PM_{10} concentrations in the Corcoran/Hanford area during the fall intensive study between 10/09/00 and 11/14/00. Sampling sites in the Corcoran/Hanford area included: Corcoran core site (COP), Santa Fe St. (SFE), grain elevator (GRA), grain elevator south (GRAS), Highway 43 (H43), and Hanford – Irwin St. (HAN).



3.3 Task 3.1.3 – Site Zone of Representation

Monitoring sites should be selected to represent several spatial scales as defined below (U.S. Environmental Protection Agency, 1997). Distances indicate the diameter of a circle, or the length and width of a grid square, with a monitor at its center.

- **Collocated or Indoor Scale or Ducted Emissions (1 to 10 m):** Collocated monitors are intended to measure the same air. Collocated measurements are often used to define the precision of the monitoring method. Different types of monitors are operated on collocated scales to evaluate the equivalence of measurement methods and procedures. The distance between collocated samplers should be large enough to preclude the air sampled by any of the devices from being affected by any of the other devices but small enough so that all devices obtain air containing the same pollutant concentrations. Effluent pipes and smoke

stacks duct emissions from industrial sources to ambient air. Pollutants are usually most concentrated in these ducts and are monitored to create emissions inventories as well as to determine compliance with emissions standards. There may be some variability across the duct that can be compensated for by longer averaging times and traverses to obtain a composite sample.

- **Microscale (10 to 100 m):** Microscale monitors are most often used to assess human exposure. These monitors show differences from compliance monitors when the receptor is next to a low-level emissions source, such as a busy roadway. Ambient compliance monitoring site exposure criteria avoid microscale influences even for source-oriented monitoring sites, while source emissions monitors avoid them because they represent emissions from a variety of sources. Microscale sites are usually operated for short periods to define the zones of representation for other sites and to estimate the zones of influence for ducted and non-ducted emitters. These sites are also used to estimate emission rates and compositions for non-ducted sources such as suspended road dust (e.g., Gillies et al., 1999).

- **Middle Scale (100 to 500 m):** Middle-scale monitors are also used for human exposure studies (e.g., Engelbrecht and Swanepoel, 1998; Watson and Chow, 2001b; Chow et al., 2002a), to evaluate contributions from large industrial facilities, and to evaluate the zones of representation of compliance sites. They are also used for process research to examine rapid changes in pollutant composition, dilution, and deposition. For air quality research, vertical resolution of pollutant concentrations on this scale (e.g., measurements on roofs of tall buildings or hilltops) elucidates mechanisms of day-to-day carryover, long-range transport, and nighttime chemistry that cannot be understood by surface measurements.

- **Neighborhood Scale (500 m to 4 km):** Neighborhood-scale monitors are used for compliance to protect public safety and show differences that are specific to activities in the district being monitored. The neighborhood-scale dimension is often the size of emissions and modeling grids used for air quality source apportionment in large urban areas, so this zone of representation of a monitor is the only one that should be used to evaluate such models. Sources affecting neighborhood-scale sites typically consist of small individual emitters, such as clean, paved, curbed roads, uncongested traffic flow without a significant fraction of heavy-duty vehicles, or neighborhood use of residential heating and cooking devices (Chow et al., 1992, 1999, 2002b; Chow and Watson, 2001).

- **Urban Scale (4 to 100 km):** Urban-scale monitors are most common for ambient compliance networks and are intended to represent the exposures of large populations. Urban-scale pollutant levels are a complex mixture of contributions from the many sources that are subject to areawide control. Urban-scale sites are often located at higher elevations or away from highly traveled roads, industries, and residential wood-burning appliances. Monitors on the roofs of two- to

four-story buildings in the urban core area are often good representatives of the urban scale (Engelbrecht et al., 1998).

- **Regional-Scale Background (100 to 1,000 km):** Regional-scale monitors are typically located upwind of urban areas and far from source emissions. Regional monitors are not necessary to determine compliance, but they are essential for determining emissions reduction strategies. A large fraction of certain pollutants detected in a city may be due to distant emitters, and a regional (rather than local) control strategy may be needed to reduce outdoor exposure. Regional-scale concentrations are a combination of naturally occurring substances as well as pollutants generated in urban and industrial areas that may be more than 100 km distant (Chow et al., 1996b). Regional-scale sites are best located in rural areas away from local sources, and at higher elevations.

- **Continental-Scale Background (1,000 to 10,000 km):** Continental-scale background sites are located hundreds of kilometers from emitters and measure a mixture of natural and diluted manmade source contributions. Anthropogenic components are at minimum expected concentrations. Continental-scale monitors determine the mixture of natural and anthropogenic contaminants that can affect large areas. The Interagency Monitoring of PROtected Visual Environments (IMPROVE) network has been used extensively in the U.S. to determine $PM_{2.5}$ compositions and their effects on visibility in National Parks and Wilderness Areas (Eldred et al., 1997).

- **Global-Scale Background (>10,000 km):** Global-scale background monitors quantify concentrations transported between different continents as well as naturally emitted particles and precursors from oceans, volcanoes, and windblown dust. These are located in isolated spots such as McMurdo in Antarctica (Mazzera et al., 2001), Mauna Loa in Hawaii (Holmes et al., 1997), and Barrow, Alaska (Polissar et al., 1999).

The zone of representation for a monitoring site is often not evident in the absence of measurements from nearby locations. To understand how $PM_{2.5}$ and/or PM_{10} varies spatially and how these spatial characteristics can be used to identify monitoring sites that are representative of overall community exposure, both temporal and spatial variations need to be examined (e.g., Kuhns et al., 1998; Blanchard et al., 1999; Chow et al., 1999, 2002b). Temporal variations across sampling periods can be calculated for each site based on the site's coefficient of variation. Spatial averages and the deviation of each site from the area-wide spatial average at all sites can be used to estimate the extent of spatial variations. Besides the basic statistics, the following activities will assist in examining and understanding the zones of influence of specific sources and the zones of representation of the receptor sites:

- Cluster analysis;

- Spatial contour plots;

- Geostatistics and kriging; and

- Successive moving average method.

Cluster analysis is a multivariate statistical procedure for detecting natural groupings in data without prior knowledge of group characteristics. This procedure has been used to determine clusters of different chemical species with similar sampling intervals (Saucy et al., 1987). Alternatively, cluster analysis can be used to determine groupings of chemical constituents based on their geographic locations. The distribution of chemical species among the satellite sites may be a result of recurring meteorological conditions or source emissions.

For a spatial cluster analysis, the data must be presented in a two-dimensional matrix consisting of the concentration measurement of a specific species for each date and site. For an unnormalized data matrix, species with high concentrations will dominate the resulting clusters. To overcome this bias, the mass and chemical data will be transformed by centering to the mean and then scaling to the standard deviation. Normalizing the data to the standard deviation allows the usage of a wide range of chemical concentrations because each trace species is given as much weight as a major component.

Several key species indicative of potential emission sources in the study area will be selected for this exercise. For example, bromine, soluble potassium, organic carbon, and elemental carbon can be chosen to represent motor vehicle and vegetative burning emissions; silicon and iron can be used to represent geological material; and sodium can be selected to represent marine aerosol (Hopke et al., 1976).

The statistical software package *SYSTAT 10* (SYSTAT Inc., Evanston, IL) allows for the use of K-means clustering to examine aerosol data. K-means clustering separates the data set into a selected number of subgroups by maximizing the variations between groups and within each group. This method is similar to one-way analysis of variance (ANOVA) in which groups are unknown and the largest F-value is sought by reassigning members to each group.

Cluster analysis using K-means follows a procedure designed to isolate the most realistic cluster groupings that have real physical meaning. K-means clustering is initially set to six possible groupings for each of the species examined. The analysis will result in a pattern of one, two, or three groupings with isolated single-site clusters. The single-site clusters will be found at the perimeter of the saturation network or along the border of a well-defined cluster. To determine whether clusters would subdivide further or retain the original grouping of sites, a second analysis is performed that eliminates the single-site clusters identified in the first analysis.

A spatial contour plot can be generated using inverse distance to a power gridding method using *Surfer 6.01* (Golden Software, Golden, CO). This method is a weighted average interpolator in which data points are weighted such that the influence of one data point relative to another declines with distance from the grid node. Normally, the inverse distance method behaves as an exact interpolator. The weighted average interpolator has a tendency to generate “bull’s eye” patterns of concentric contours around the data points, and

a smoothing parameter can be assigned to generate the contour plot. Figure 3.1-4 illustrates an average PM_{10} concentration contour plot for 10 fall intensive sites (excluding the Hanford site) within a 5.5 km N-S by 4.5 km W-E study domain. The zone of influence for the cotton handling operation (SFE) is small, with PM_{10} concentrations decreasing by ~20% to 35% within 1 km. This zone would be smaller yet if additional samplers had been located near the gradient site. The zones of influence of grain elevator operations (represented by the GRA and GRAS sites) and unpaved roads (represented by the CO5 site) near the Corcoran site are also small, with ~20% decreases in PM_{10} concentrations within 0.5 to 0.7 km. Chow et al. (1999) also found that zones of influence around individual fugitive dust emitters were less than 1 km in the Las Vegas Valley. Many of these contour plots will be generated for individual days and for specific PM constituents to examine the extent of site representation.

Geostatistics and kriging were developed in the early 1960's for the estimation of ore reserves in the mining industry. This technique has more recently been extended to include several disciplines in the earth (Juang and Lee, 1998), hydrological (Chang et al., 1998), and atmospheric sciences (Shindo et al., 1990; Schaug et al., 1993; Casado et al., 1994; Zekai, 1995; Buckley, 1997; Stedman et al., 1997), and is suited to any spatial or three-dimensional data sets.

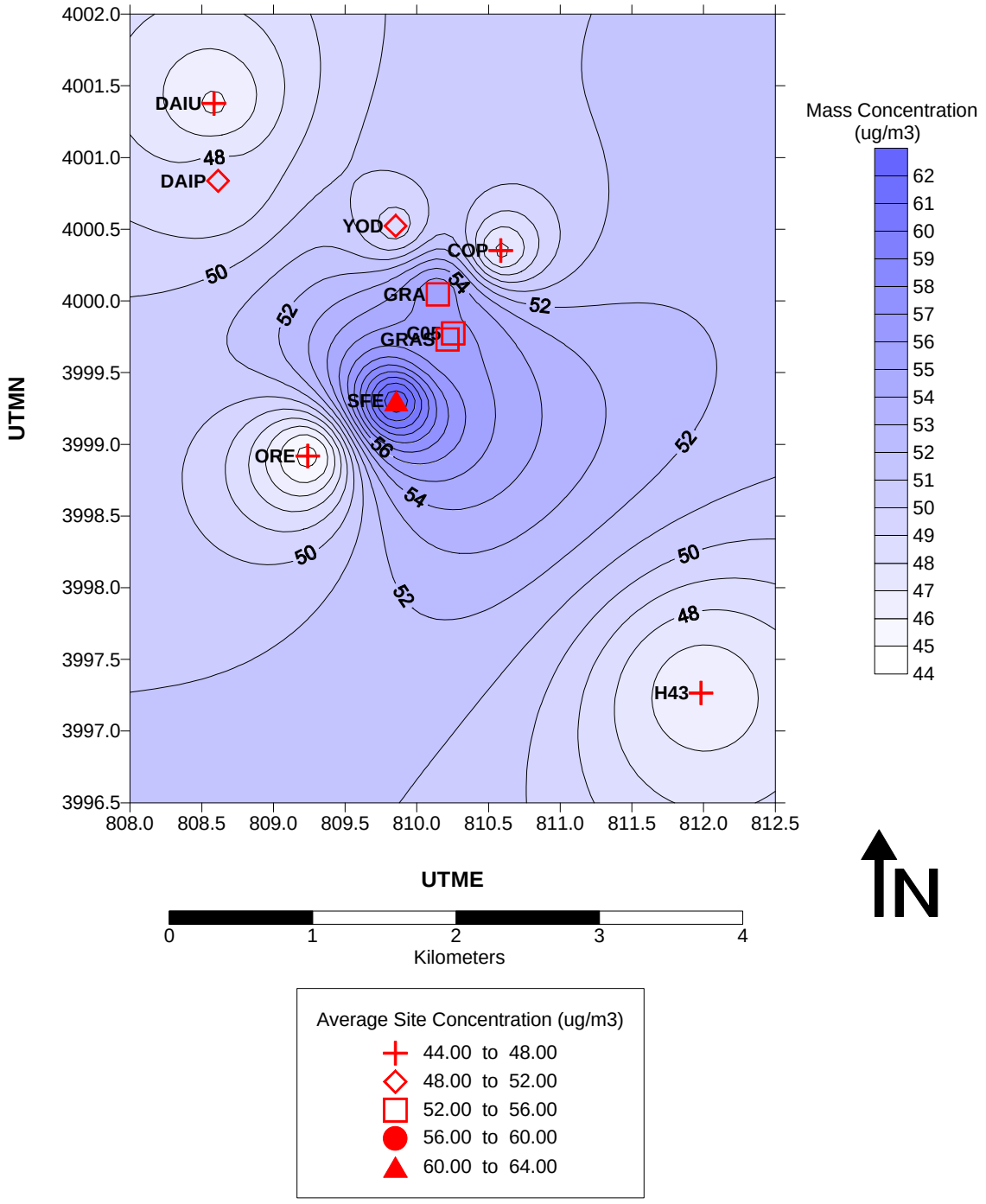
The objectives of geostatistical estimation for this analysis are:

- To characterize and interpret the behavior of aerosol measurements; and
- To apply the interpretation to predict likely values for specific variables at locations which have not been sampled.

The technique allows for the estimation of pollutant concentrations in a three-dimensional space based on the measured values at the satellite and anchor sites. The correlation of various PM constituents can be modeled by this technique. The input to kriging is a model fitted to the experimental variograms calculated from measurements at the monitoring sites. This technique can be applied to both two-dimensional site coordinates and three-dimensional (site coordinates and time) data sets so that temporal and spatial variations can be simultaneously considered. Spatio-temporal data sets can be applied to construct pollutant maps for key air quality variables for each day or part of the day. This analysis, which is performed with *Ecological Spatial Statistical Evaluation* software (Ecosse North America, Columbus, OH), will demonstrate that the technique can be used to obtain an accurate image of the state of the atmosphere in the San Joaquin Valley at a given time, and also variations with time. This information can be applied to:

- Define optimal sampling strategies;
- Construct variogram maps to best show the distribution of pollutants; and
- Identify domains (regions) exceeding critical thresholds and standards by using non-linear kriging techniques.

Figure 3.1-4. Concentration contours of average PM_{10} mass at the Corcoran site for the period from 10/09/00 to 11/14/00. The 10 included sites are: Santa Fe St. (SFE), Corcoran railroad shoulder (CO5), Corcoran core site (COP), paved Dairy Road (DAIP), unpaved Dairy Road (DAIU), grain elevator (GRA), grain elevator south (GRAS), Highway 43 (H43), Oregon Avenue (ORE), and Yoder Street (YOD).



Cluster analysis, spatial contour plots, and geostatistics and kriging may complement one another to confirm a site's zone of representation. If an FRM site in the compliance network is located in a cluster of CRPAQS satellite sites, the same technique can be used to examine the FRM site's representation.

The successive moving average method illustrated by Watson and Chow (2001b) is illustrated in Figure 3.1-5. In this method, nearby sources show peaks superimposed on a smoothly varying background. These peaks are removed by interpolating between values on either side of the peak. The removed peaks are summed over desired averaging period, 24 hours in the illustration, to estimate middle-scale contributions. Urban-scale contributions are determined by difference between peak-free measurements at urban (FSF) and regional scale monitors (HELM). Several regionally representative monitors would be averaged, after local peak subtraction, to compare against urban monitors.

Both these temporal and spatial methods are needed because of the diversity of measurements available in CRPAQS. In the satellite network, only 32 of the 53 24-hour $PM_{2.5}$ and/or PM_{10} measurement sites are accompanied by nephelometers acquiring particle light scattering as $PM_{2.5}$ surrogates. A list of sites where both PM mass and nephelometer measurements were made can be found in Table 1.1-6 of DRI's proposal for Task 1.1.

3.4 Task 3.1.4 – Siting Characteristics

Locating PM monitors requires consideration of internal and external criteria. Internal requirements are those for operating the needed instruments (e.g., long-term site commitment, sufficient operating space, access, security, safety, power, and environmental control), while external criteria address site surroundings to achieve specific monitoring purposes. External siting criteria differ depending on the zone of representation intended for a specific monitoring site (Watson et al., 1997). The following criteria will be evaluated with respect to:

- Exposure. Monitors should be located >20 m from nearby trees, and twice the difference in elevation difference from nearby buildings or other obstacles.

- Distance from nearby emitters. The monitor should be outside the zone of influence of sources located within the designated zone of representation for the monitoring site. Neighborhood and urban zones of representation are needed for community-oriented compliance monitors. These should generally be at least 1 km from very large, visibly identifiable source areas. Figure 3.1-6 provides guidance on the recommended monitoring distances from paved roads with different levels of average daily traffic for neighborhood- and urban-scale sites. A minimum distance of ~50 m from busy paved highways is usually outside the road's immediate zone of influence for a rooftop monitor. For larger than middle-scale monitoring, no unpaved roads with significant traffic or residential wood-burning appliances should be located within 100 m of the monitoring location. Background monitoring sites should be located >100 km from large population centers, and >100 m from roads and wood burning (burning is common, though often intermittent, in camping, forested, and agricultural areas).

Figure 3.1-5. Example of the successive moving average method to separate local from regional contributions at the HELM site and local from regional plus urban contributions at the FSF (Fresno First Street) site. The peaks in the nephelometer trace are attributed to middle-scale source contributions. The lower panel shows regional, urban, and middle scale contributions to 24-hour $PM_{2.5}$ at Fresno.

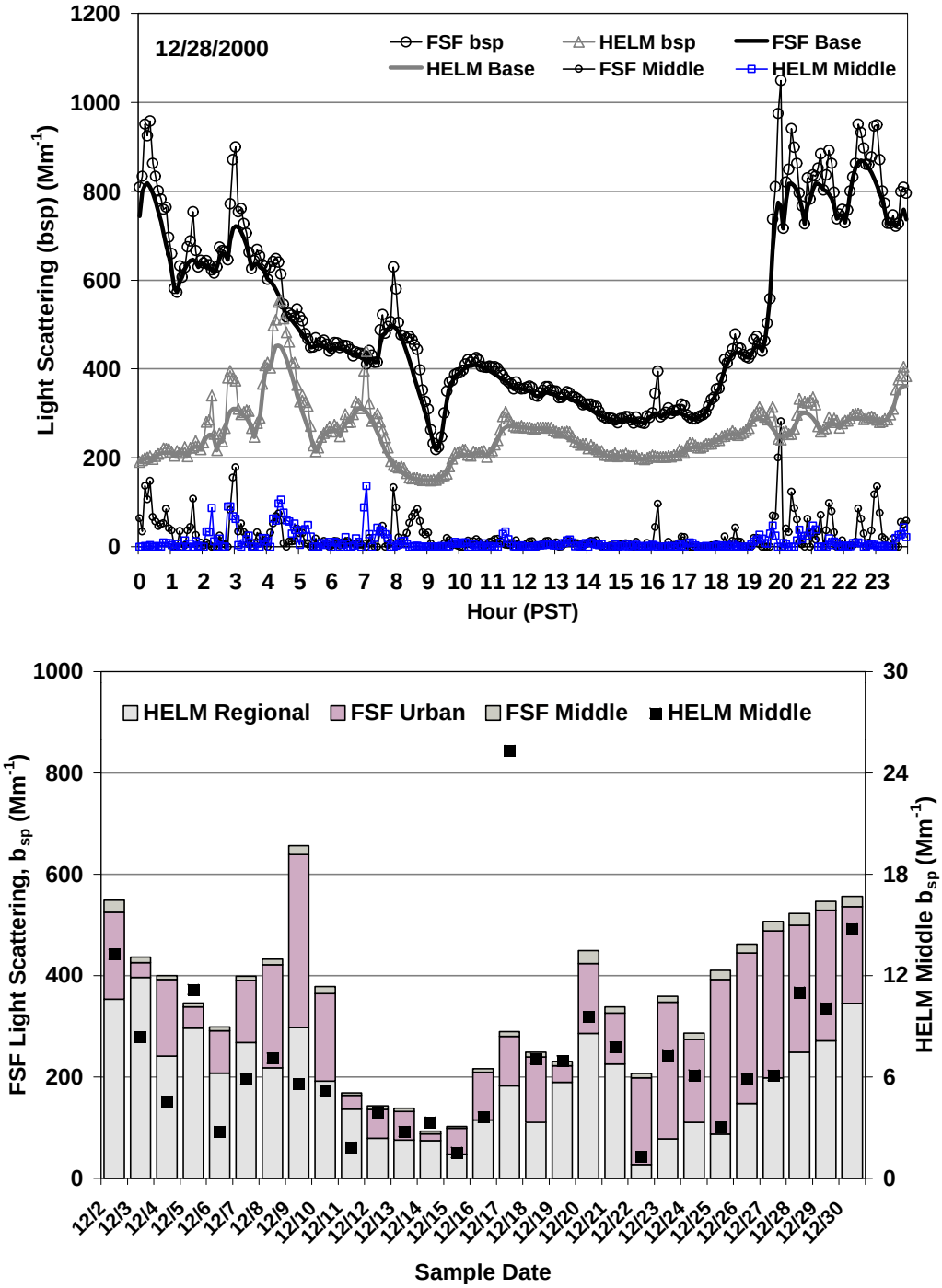
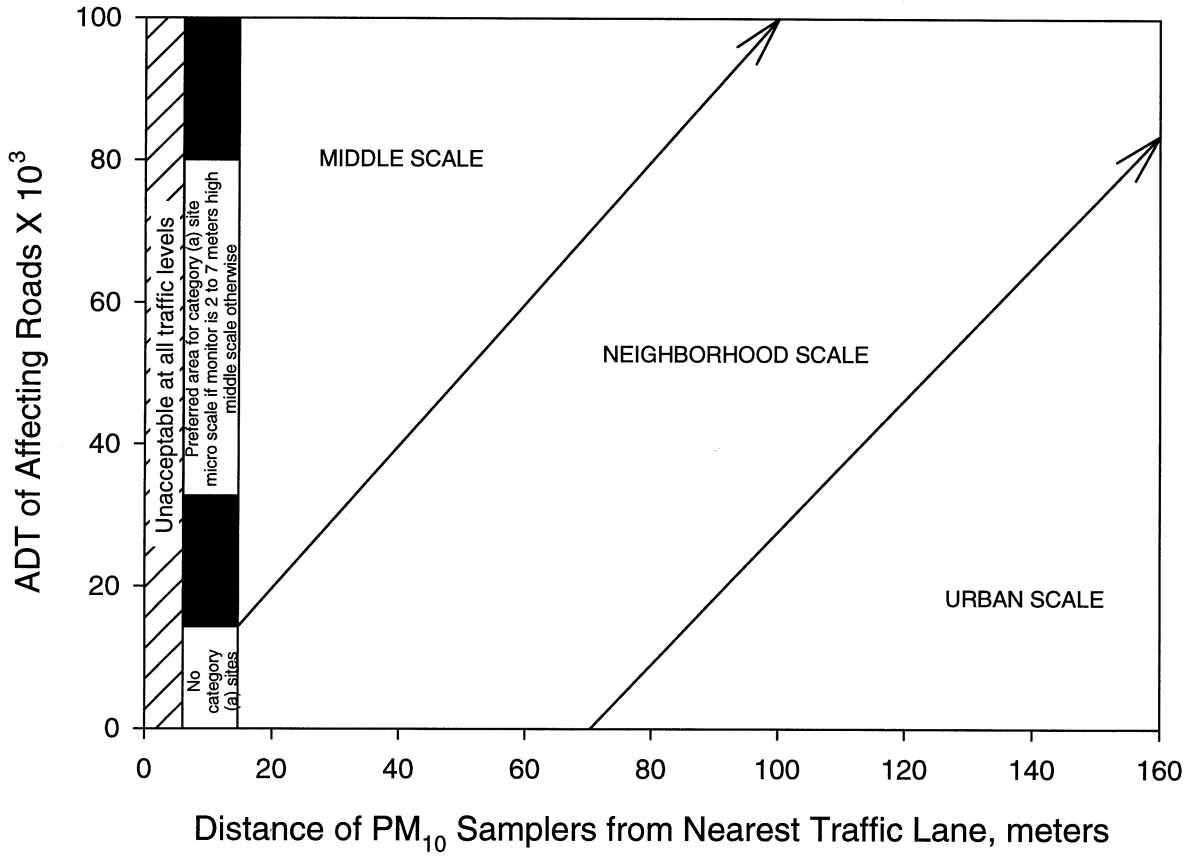


Figure 3.1-6. Recommended distances and elevations of PM sampler inlets from heavily traveled roadways.



- Proximity to other measurements. Other air quality and meteorological measurements can aid in the interpretation of high PM levels. For example, high local wind gusts may explain high PM readings as caused by wind blown dust. These gusts are often localized, and would not be detected on a more distant monitor. Similarly, a strong correspondence between hourly CO and PM readings would indicate that locally emitted vehicle exhaust is a large contributor at that site. This conclusion would be more tenuous if the CO measurements were not collocated. In particular, collocating PM_{10} and $PM_{2.5}$ monitors will provide information on the size distribution of suspended particles.

Emission and meteorological data are needed to further confirm the zones of representation of each site. Emission inventories, emission microinventories (if available), maps of the surrounding geography (4 km^2), land use records, visual observations, logs of every-sixth-day area surveys, local event calendars (e.g., agricultural field burning/tilling, track racing) and any other emission characteristics acquired during the study will be examined. Case studies will be conducted to find the causes of standard exceedances and to characterize specific pollution build-up and clearing periods. These findings, along with annual and seasonal averages, spatial and temporal coefficients, and primary and secondary source contributions, will be used to summarize siting characteristics required for the network.